W. R. GRACE & CO.

RESEARCH DIVISION

Washington Research Center, Clarksville, Maryland 21029

SYNTHESIS OF LINEAR, DOUBLE CHAIN LADDER POLYMERS FROM SUBSTITUTED TETRAPHOSPHONITRILES

Final Report

Covering the Period

May 3, 1966 through May 15, 1967

By:

Bernard Grushkin, Principal Investigator

and

Robert M. Murch
Thomas Bieniek
Theodore S. Soddy

Contract No. NASw-1415
SC No. 10-9197
Control No. 21-055-001-(003)

W. R. GRACE & CO.

RESEARCH DIVISION

Washington Research Center, Clarksville, Maryland 21029

September 12, 1967

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812
Attn: R-P&VE-MNP

Gentlemen:

Attached is the Final Report for NASw-1415 for the period of May 16, 1966 to May 15, 1967.

R. M. Murch
Senior Research Chemist

RMM:jk

ABSTRACT

A study of the thermal deammoniation of β-trans-$[\emptyset PN(NH_2)]_4$ was made. The highest molecular weight polymers (36000) were obtained when the reaction was conducted at 265°C. Satisfactory polymers were not obtained when the condensation was conducted in a high-boiling solvent.

The preparation of several new β-trans-tetraphenylcyclotetraphosphonitriles was accomplished. Among those prepared were tetraazide, a tetramethylamino, a tetraisothiocyanate, and a tetramethoxymethylamino. Brief studies of the thermally induced polymerizations of the tetraazide and tetramethylamino cyclics were made. Neither cyclic led to polymers with desirable properties.

Attempts to copolymerize β-trans-$[\emptyset PNCl]_4$, with toluene 2,4-diisocyanate, with pyromellitic tetraacid chloride, and with pyromellitic dianhydride were conducted. No high-molecular weight polymers having desirable properties were obtained from these copolymerizations.

During the study of the thermally induced deammoniation of β-trans-$[\emptyset PN(NH_2)]_4$ a new type of polymer was discovered. Polymers containing transition metal cations (Cu^{++}, Co^{++}, Ni^{++}, Fe^{++}) coordinated with the tetraaminophosphonitrile cyclics have been prepared. A preliminary study of the chemical and physical properties of these new polymers was made.

OBJECTIVE OF THE PROGRAM

The ultimate objective of this investigation is to prepare a new class of double-bridged, ladder polymers from cyclic tetrameric phosphonitriles. Successful ladder polymers are expected to be thermally stable beyond present day capabilities.

Of the four possible isomers of $[\emptyset PNCl]_4$, three would be suitable for the preparation of ladder polymers. One of these, the β-trans-isomer, can be synthesized in good yield. Thus, one objective of the program has been to prepare and characterize polymers from the β-trans isomer.

Realizing the possible limitations of having phenyl groups on a phosphonitrilic polymer, a second objective of this program has been the preparation of new monomers, particularly $[CH_3PNCl]_4$, from which ladder polymers would be prepared and characterized.

SUMMARY AND CONCLUSIONS

Thermal polymerization of β-trans-$[\phi PN(NH_2)]_4$ yields a polymer with a degree of polymerization of approximately 70 units. The polymer decomposes at about 400°C by loss of phenyl groups. Furthermore, small amounts of water can slowly hydrolyze the polymer if it is heated in a solvent.

Thermal treatment of β-trans-$[\phi PN(NHCH_3)]_4$ does not give a well defined polymeric product. Elimination of di- and trimethylamine during polymerization implies that a complex polymeric resin is produced. No suitable method has been found to obtain high-molecular weight polymers from the cyclic phosphonitrile.

Polymers produced by the thermal deammoniation of β-trans-$[CH_3PN(NH_2)]_4$ have been produced but these polymers are not thermally stable above about 300°C.

A new type of polymer system was discovered during the experiments in polymerization of phosphonitrilic tetramers. These new polymers are coordination polymers containing alternate β-trans-$[\phi PN(NH_2)]_4$ units and transition-metal salt units. Polymers with $CuSO_4$, $CuCl_2$, $CoCl_2$, $NiCl_2$ and $FeCl_2$ have been prepared. These polymers have the transition-metal cation associated with the pendant amine groups in the β-trans-$[\phi PN(NH_2)]_4$ units, but upon thermal deammoniation, the metal cation becomes associated, at least partially, with the phosphonitrile ring nitrogens. The deammoniated polymers apparently have an enhanced thermal stability, but at this time, very little is known about their structure or properties.

RECOMMENDATIONS

1. Further work on polymers from β-trans-$[\phi PN(NH_2)]_4$ does not appear justified. Any future work of this type should be designed around polymers with phenoxy groups in place of the phenyls and possibly oxygen bridges in place of the secondary amino links between cyclic phosphonitriles.

2. An investigation of the coordination polymers containing cyclic phosphonitriles and transition-metal salts should be made. This new polymer system has shown preliminary promise as a high-temperature polymer. A relatively simple program to evaluate the parameters in this system should be conducted.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

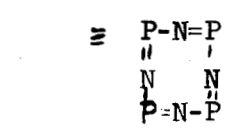
The work on this contract was based on the concept that a tetrafunctional phosphonitrilic tetramer could be condensed to a doubly-bridged ladder-type polymer.

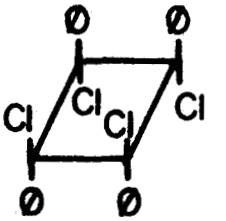
During the first year of the contract, the four tetrameric products from the reaction,

$$x\text{Ø}PCl_4 + xNH_4Cl \rightarrow \frac{x}{4}[\text{Ø}PNCl]_4 + 4x\ HCl$$

were structurally characterized. The major tetrameric product was found to have the following structure:

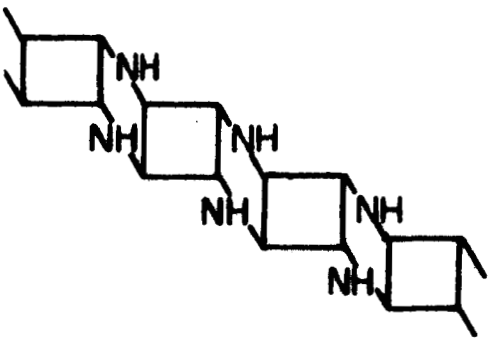
≡





β-trans-$[\text{Ø}PNCl]_4$

Based on this structure, the following type of polymer might be expected.



The polymerization of β-trans- tetraaminotetraphenylcyclotetraphosphonitrile was accomplished by a thermally induced deammoniation at 260°C. Soluble polymers with a molecular weight of 20,000 were obtained but attempts to prove the existence of a ladder-like structure were not conclusive. The elimination of benzene from this polymer occurs when it is heated above 400°C.

During the second year of the contract, an investigation of similar polymers containing methyl groups instead of phenyl groups was conducted. The synthesis of non-geminal tetraaminotetramethylcyclotetraphosphonitriles was attempted by the following sequence,

(1) $[PNCl_2]_4 \xrightarrow{Me_2NH} [(Me_2N)\ PnCl]_4$

(2) $[(Me_2N)\ PNCl]_4 \xrightarrow{MeMgBr} [(Me_2N)PNMe]_4$

(3) $[(Me_2N)\ PNMe]_4 \xrightarrow{HCl} Me_2NH.HCl + [MePNCl]_4$

(4) $[MePNCl]_4 \xrightarrow{NH_3} [MePNNH_2]_4 + NH_4Cl$

but the products from this sequence could not be readily isolated. This approach was abandoned in favor of the synthesis,

$$xMePCl_4 + xNH_4Cl \rightarrow [MePNCl]\ x + {}_4x\ HCl$$

The methylchlorocyclics were prepared in low yields and proved to be hydrolytically unstable.

Polymers derived from $[MePn(NH_2)]x$ did not have improved stability and, therefore, work on this system was discontinued.

The work reported in this report is essentially a continuation of this study. Efforts during the third year have been directed towards preparing higher molecular weight polymers from β-trans-$[\emptyset PN(NH_2)]_4$. Polymers with molecular weights of 40,000 (DP=80) were prepared and several methods of polymerization were investigated.

Also discussed in this report is the synthesis of new coordination polymers that presumably contain alternating tetrameric phosphonitrile units and transition metal halides.

RESULTS AND DISCUSSION

I. Phenyl Phosphonitriles

A. Preparation of Derivatives of β-trans-$[\emptyset PNCl]_4$

1. β-trans-$[\emptyset PN(NH_2)]_4$:--Ammonolysis of β-trans-$[\emptyset PNCl]_4$, when carried out in chloroform or benzene, results in the formation of two products, α-trans- and β-trans-$[\emptyset PN(NH_2)]_4$, in about equal amounts. However, the same reaction if carried out in tetrahydrofuran gives only β-trans-$[\emptyset PN(NH_2)]_4$ [1].

The reaction of β-trans-$[\emptyset PNCl]_4$ with ammonia, in THF, was carried out a number of times. Results of some of these runs is summarized in Table I. In each case the yield of β-trans-tetrakisamide exceeded 75%. An infrared spectrum of the product is shown in Figure 1.

TABLE I

Synthesis of β-trans-$[\emptyset PNNH_2]_4$

Starting $[\emptyset PNCl]_4$		$[\emptyset PNNH_2]_4$			Residue	
Weight, g.	m.p., 0°C	Weight, g.	m.p., °C	%Yield	Weight, g.	m.p., °C.
3.0	234-8	2.75	224-5	92	-	-
49.0	234-8	8.3	222-4			
		19.0	221-2	78	5.2	<215
		8.2	220-3			
50.1	234-8	18.3	222-3			
		9.1	219	75	6.5	214-7
		6.0	221-2		2.5	<210
51.0	234-8	17.8	223-4			
		9.8	221-2	86	6.5	<210
		10.8	219-20			

2. β-trans-$[\emptyset PN(N_3)]_4$

Preparation of the non-genimally substituted tetraazide was reported previously [2]. Polyazide derivatives are stable only if substitutions are non-geminal. They are unstable if two azido groups are attached to a single phosphorus atom [3]. The non-geminal tetraazide can be prepared

by simple nucleophilic substitution of an azido group for chlorine.

(1) $$4NaN_3 + [\emptyset PNCl]_4 \rightarrow [\emptyset PN(N_3)]_4 + 4NaCl$$

Mild heating of an acetonitrile solution of $[\emptyset PNCl]_4$ in the presence of excess sodium azide causes the reaction to go to completion in only a few hours. In this way β-trans-$[\emptyset PN(N_3)]_4$, m.p. 134-5°, was prepared in 87% yield. It is assumed that the β-trans configuration was maintained since no other isomers were recovered. An infrared spectrum (Figure 2) shows the characteristic azide absorption band at about 2100 cm^{-1}.

3. $[\emptyset PN(NCS)]_4$:-- Preparation of isothyocyanate derivatives also is a relatively simple procedure. It has been reported that the ambident thiocyanate anion, $N\equiv C\text{-}S^-$, can react with phosphonitrilic chlorides to give the corresponding isothiocyanate phosphonitriles, e.g., $[PN(NCS)_2]_n$.[4] Hexaisothiocyanato phosphonitrilic trimer can in turn be reacted with amines to give $[PN(NHCSNHR)_2]_3$.[5]

β-trans-$[\emptyset PN(NCS)]_4$ was prepared by treating β-trans-$[\emptyset PNCl]_4$ with an excess of KSCN in refluxing acetonitrile. Metathesis occurred slowly as the reactants were heated. An essentially quantitative yield of product was obtained. The product, m.p. 145-7°, has an infrared spectrum as shown in Figure 3.

4. β-trans-$[\emptyset PN(NHCH_3)]_4$:-Preparation of the β-trans-tetrakis-monomethylamide was reported previously.[1] The compound is prepared by passing excess methylamine through a tetrahydrofuran solution of β-trans-$[\emptyset PNCl]_4$. The compound melts at 148-150°C. and is obtained in approximately 50% yield.

5. $[\emptyset PN(NHCH_2OCH_3)]_4$: - In an attempt to prepare a monomer that would undergo low temperature polymerization reactions, β-trans-$[\emptyset PN(NH_2)]_4$ was treated with aqueous formaldehyde in refluxing methanol.

(2) $$[\emptyset PN(NH_2)]_4 + 4CH_2O + 4MeOH \rightarrow [\emptyset PN(NHCH_2OCH_3]_4 + 4H_2O$$

The product isolated from this reaction gave the following elemental analysis:

Found: C, 54.69; H, 6.18; N, 15.32; P, 16.97; [O], 6.84.

The empirical formula is $C_{33.3}H_{45.2}P_4N_{7,9}O_{3,12}$.
It is believed that the product contains $-NHCH_2OCH_3$ groups. The strong IR absorption band at about 1060 cm^{-1} (Figure 4) may be attributed to-C-O-C-.

The reaction was repeated using paraformaldehyde as a source of anhydrous formaldehyde. The reaction was carried out in anhydrous methanol. Recovered product analyzed similarly to that of the first reaction.

Found: C, 54.39; H, 6.01; N, 14.73; P, 16.15; [O], 8.72.

The calculated empirical formula for this product is $C_{34.8}H_{45.7}P_4N_8O_4$.

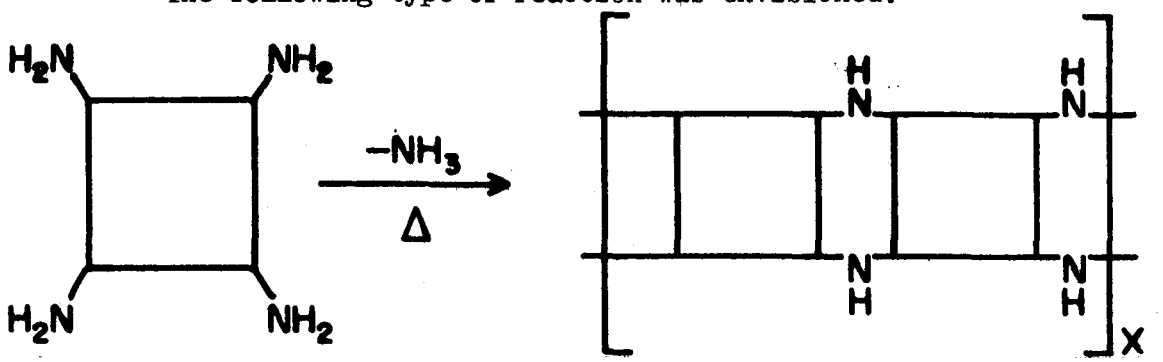
B. Preparation of Polymers from Phenyl Phosphonitriles

1. Thermal Deammoniation of β-trans-$[\phi PN(NH_2)]_4$

Thermal deammoniation of β-trans-$[\phi PN(NH_2)]_4$ to yield polymers was reported previously. [1]

The following type of reaction was envisioned:

(3)



Ideally, for each mole of monomer there should be obtained no more than half a mole of NH_3.

A study was conducted to determine if the molecular weight distribution of the polymer is a function of the temperature at which condensation occurs. Deammoniations were carried out at temperatures ranging from 209 to 320°C. The data are summarized in Table II. The percent ammonia evolved is based on that expected for reaction 3. Ammonia half-life is that time required to eliminate fifty percent of the expected ammonia. The polymerized product was then dissolved in 75 ml. of anhydrous chloroform and stirred overnight. That part which was soluble was used for further analysis. Molecular weights that were determined for the total product soluble in chloroform were fairly low. Higher molecular weight polymer, however, was recovered by fractionally precipitating the chloroform soluble polymer. The initial precipitate, representing from 13 to 24 percent of the total chloroform soluble material, was used for a second molecular weight determination. The highest molecular weight obtained was 36,000, which represents a DP of about 70 tetramer units. It can be seen that the highest number average molecular weights were obtained when the polymerization was carried out at about 265°C. Although over 90% of the available ammonia is evolved at higher temperatures, lower molecular weight polymer results. This behavior might be explained by the formation of cyclic ladders on the cleavage of phosphonitrile cyclics to form viscous, highly cross-linked resins of lower net molecular weight.

Thermal polymerization was tried in a high-boiling solvent. β-trans-Tetraamide was dissolved in diphenylmethane (b.p. 260°C.) and heated to reflux. The rate of ammonia evolution was essentially the same as that observed for the melt reaction. Ninety percent of the ammonia was evolved as expected for reaction 3. Molecular weights of polymer fractions recovered from the ϕ_2CH_2 indicated that polymerization did not progress beyond the coupling of about four tetrameric units.

TABLE II

Thermal Deammoniation of β-trans-$[\emptyset PNH_2]_4$

Run No.	Temp. (°C)	NH_3 Evolution ½ Life (Hrs.)	NH_3 Evolution Yield %	Overall Product % Sol In $CHCl_3$	Overall Product Mol.Wt	High Mol. Wt. Product Wt %	High Mol. Wt. Product Mol.Wt.
Prev. Typical	209	-	86	55	5,900	23	11,700
Prev. Best	219	-	75	92	13,000	13	20,000
4046-32	230	6.5	92	37	1,050	-	-
4046-33	260	3.0	96	71	2,800	18	7,150
-36	265	1.8	100	34	2,000	24	7,200
-39	265	0.5	92	84	-	18	-
-40	265	0.5	89	94	-	31	22,000
-42	265	0.5	90	95	(Sample decomposed)		
-46	260	0.5	89	59	3,750	15	35,000
-47	280	0.1	90	90	3,750	14	25,800
-48	300	0.05	90	92	1,780	13	4,260
-49	320	0.03	94	100	2,030	13	4,500

Structural characterization of the polymer could not be accomplished since an accurate determination of the ratio of NH_2/NH or NH_2/ϕ could not be made.

As pointed out previously, [1] polymers derived from phenyl phosphonitriles evolve benzene at about 400°C. We now believe that these polymers also depolymerize in the presence of small amounts of water.

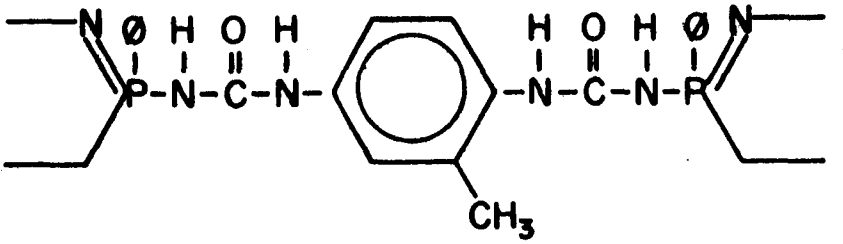
Polymer (20,900 mol. wt.) resulting from the thermal deammoniation of β-trans-$[\phi PN(NH_2)]_4$ was refluxed in anhydrous methylene chloride and reagent grade chloroform. In each case molecular weights decreased substantially to about 10,000 to 15,000. It is suspected that trace amounts of atmospheric moisture absorbed by the solvent or by the polymer itself caused hydrolysis accompanied by a decrease in molecular weight.

In another experiment polymer of 20,900 molecular weight was heated at 300°C. in the absence of solvent in a stream of dry nitrogen. The resulting ammonia evolution was in excess of $-NH_2$ groups calculated to be present. The residue, after heating, had a molecular weight that was lower than that of the starting material. The experiment was repeated at 265°C with the same results. No clue as to the cause of degradation was observed in the IR spectrum of the degraded polymer.

It is probable that the cause of degradation in all of these experiments is hydrolysis as caused by trace amounts of water. The latter runs, carried out in the absence of any solvent, serves to pinpoint the source of water to the polymer itself. Presumably the polymer can absorb enough water to lead to depolymerization upon heating. This would account for the excessive evolution of ammonia when the polymer, containing only a small number of NH_2 groups, is reheated at 300°C.

2. Reaction of β-trans-$[\phi PN(NH_2)]_4$ with Toluene-2, 4-Diisocyanate

The condensation of amines with diisocyanates is well known. We have attempted the polymerization of $[\phi PN(NH_2)]_4$ with toluene-2,4-diisocyanate in an effort to form the following type of bridging groups.



Upon addition of two equivalents of toluene diisocyanate to the tetraamide in xylene a precipitate formed which, upon separation, had the following elemental analysis.

Found: C, 56.40; H, 4.76; N, 18.84; P, 10.70; [O], 9.30 (diff.).

for $C_{15}H_{15}N_5PO_2$: C, 54.85; H, 4.62; N, 21.35; P, 9.42; O, 9.78.

This material does not melt at 300°C. Molecular weights could not be determined because of the insolubility of the polymer in a variety of organic solvents.

3. Coupling with β-trans-[ØPNCl]$_4$

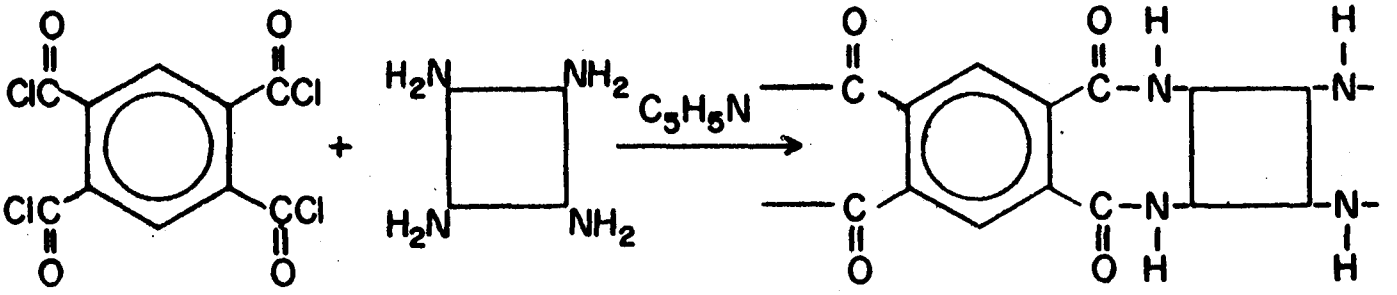
The possibility of using the largest polymer obtained to date as a prepolymer was investigated. We had hoped to couple ladders with a variety of di- or tetrafunctional molecules and thereby significantly increase the molecular weights.

The first attempt was made by refluxing a polymer sample (mol. wt. 20,900) with a stoichiometrically equivalent amount of β-trans-[ØPNCl]$_4$ in methylene chloride. The mixture was held at reflux for 24 hours. After working up the mixture a sample of amide polymer was recovered that had a molecular weight of 1,320. A similar result was obtained when the reaction was repeated; however, the phosphonitrile amide polymer now had a molecular weight of 3,380. An infrared spectrum for the final product is shown in Figure 5. Positive identification of the strong absorption peak at 1650 cm.$^{-1}$ has not been made; however, interaction of the solvent with the polymer may have led to the formation of -N=CH_2 bonds which would account for the observed spectrum.

The depolymerization is probably due to hydrolysis by trace amounts of water. This was noted in an earlier section.

4. Reaction of Pyromellitic Tetraacid Chloride (PMTC) with β-trans-[ØPNNH$_2$]$_4$.

Acid chlorides can react quite smoothly with amides if one first prepares the pyridine complex.[6] The expected reaction of PMTC with β-trans-tetrakisamide is as follows:



Addition of pyridine to PMTC in chloroform resulted in the formation of a blood-red soluble complex. Upon refluxing this complex with β-trans-tetrakisamide a solid precipitated after several hours. An infrared spectrum of the product (Figure 6) does not have the expected absorption at about 1600 cm.$^{-1}$; however, there is a shift in the band from 900 cm.$^{-1}$ to 960 cm.$^{-1}$. Also present is a fairly strong absorption peak at 2650 cm.$^{-1}$ which is usually attributed to P-OH. The product isolated from this reaction

analyzed very well for $[\emptyset PN(NH_2)]_4.3HCl$.

Found: C, 43.45; H, 4.82; N, $\begin{matrix}17.08\\16.90\end{matrix}$; P, $\begin{matrix}18.74\\18.55\end{matrix}$; Cl, 15.88.

Calc'd for: $C_{24}H_{31}N_8P_4Cl_3$: C, 43.60; H, 4.73; N, 16.45; P, 18.72; Cl, 16.08.
No polymeric product containing the pyromellitic acid group was isolated.

5. Reaction with Pyromellitic Dianhydride (PMDA)

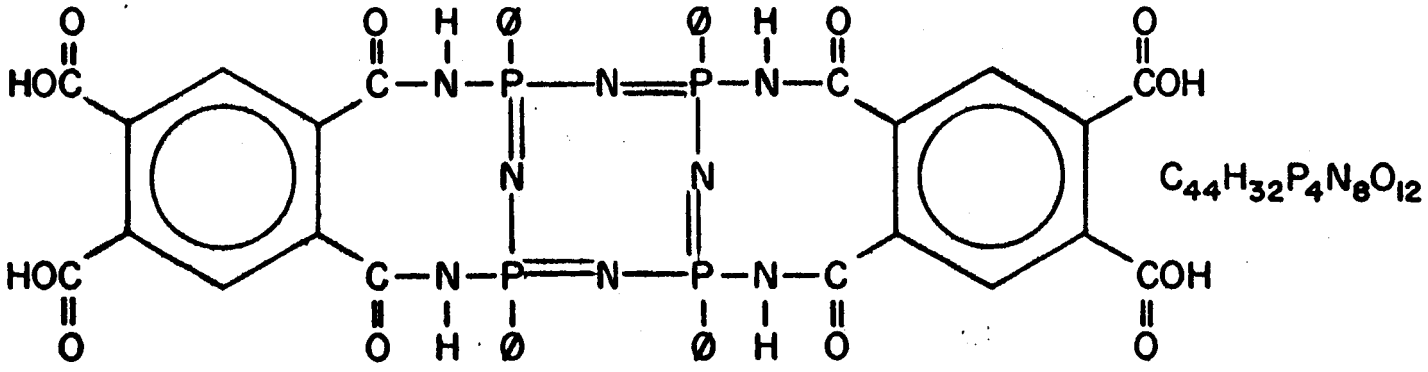
Four reactions were carried out in which an equimolar amount of PMDA was reacted with the tetraamide in DMF. The first reaction, reported previously, resulted in the isolation of a material which had a molecular weight of approximately 1,400.

In an effort to prepare polymers of higher molecular weight, two reactions were carried out at reflux wherein one reagent was slowly added to the other. Water, formed as a by-product, was continually removed by distillation. In both cases, a black insoluble resinous solid remained after vacuum distillation of the DMF. The solids are not readily soluble in common organic solvents and appear to be somewhat hygroscopic. Elemental analyses of both materials are as follows:

Found: A: C, 49.19; H, 4.82; N, 11.38; P, 12.86; [O], 21.65 diff.

B: C, 51.70; H, 5.44; N, 11.4; P, 12.35; [O], 19.11 diff.

Empirical formulae for both materials are: for (A) $C_{40}H_{46.8}P_4N_8O_{12}$; for (B), $C_{42.8}H_{54}P_4N_8O_{12}$; which can be approximated by the following unit.



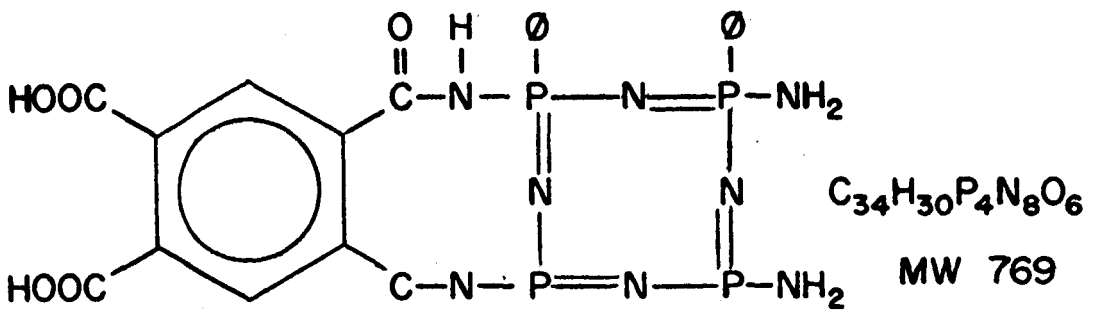
The reaction of PMDA with the tetraamide in DMF at room temperature yielded a light-tan solid that was partially soluble in chloroform.

Found: C, 48.19; H, 4.64; N, 12.44; P, 12.43; O, 22.3 (diff.)

Based on this analysis, the empirical formula is $C_{40}H_{46}P_4N_8O_{14}$. The chloroform soluble fraction, however, analyzed as follows:

Found: C, 52.65; H, 5.47; N, 12.28; P, 17.44; [O], 12.16 (diff.)

The empirical formula is $C_{31.3}H_{39.04}N_{6.2}P_4O_{5.4}$. An infrared spectrum of this material is shown in Figure 6. The molecular weight, determined by VPO in chloroform, was 830. The soluble reaction product may be primarily the following:



It can be concluded that the reaction of PMDA with tetraamide results in the formation of very low molecular weight polymers that are relatively insoluble and difficult to characterize.

C. Polymers of β-trans-$[\text{ØPN(NHCH}_3)]_4$

1. Thermal Polymerization of β-trans-$[\text{ØPN(NHCH}_3)]_4$

Thermal polymerization of β-trans-$[\text{ØPN(NHMe)}]_4$ requires higher temperatures than does the polymerization of the analagous tetraamide. Table III shows results obtained for the thermal deamination of $[\text{ØPN(NHMe)}]_4$.

TABLE III

Thermal Polymerization of β-trans-[ØPN(NHMe)]$_4$

Temp.(°C.)	CH_3NH_2 Half-Life	Evolved Yield Amine	% Prod. Sol. in $CHCl_3$	Mol. Wt. Prod.	Mol. Wt. Highest cut(s)
305	6	86	100	1,570	8,780
310	3.8	77	90	1,760	11,000
335	2	85	100	1,820	5,150-8,140
350	0.5	80	25	3,250	17,090-16,000
375	0.5	80	7%	2,030	-
400	0.3	73	5	690	-

Polymerizations were carried out by heating the cyclic tetramer under a stream of nitrogen. Evolved gas was passed into water and continually titrated with acid. In this manner the progress of the reaction was followed. After completing the deamination, the residue was taken up in chloroform and fractions precipitated with n-hexane. The first fraction contained the highest molecular weight material.

Several of the lower molecular weight samples were examined by proton NMR spectroscopy. In each case the peak attributed to methyl groups was too broad to distinguish different methyl group environments. The broadness and lack of detail of the methyl absorption persisted after D_2O exchange and P^{31} decoupling. It was noted also that the phenyl proton to methyl proton ratio was too high. In one instance the phenyl proton/methyl proton ratio was 7.1/1. For a high molecular weight polymer, this ratio should approach 3.3/1. The low methyl content of the polymer was confirmed by elemental analysis.

Found: C, 55.26; H, 5.15; N, 15.21; P, 23.14.

The empirical formula derived from the above elemental analysis is $C_{24.6}H_{27}N_6P_4$. If it is assumed that no benzene is lost during polymerization, then the $Ø/CH_3$ ratio is 6.6/1.

In order to determine the nature of the deamination products a run was made in which 3.854 g. of β-trans-[ØPN($NHCH_3$)]$_4$ was heated at 300°C. in a stream of dry helium. All volatile products were collected in a liquid nitrogen trap. The reaction was stopped at the end of 5 hours. The weight lost by the sample was 0.68 g.; that recovered in the trap was 0.62 g. or 92 percent of the volatiles. Results of mass spectral analysis of the volatiles are given in Table IV.

TABLE IV

Analysis of Thermal Deamination
Products of β-trans-$[\emptyset PN(NHCH_3)]_4$

Found	Mole %	g.
methylamine	42.3	0.217
dimethylamine	11.7	0.093
trimethylamine	17.5	0.184
ammonia	24.8	0.074
benzene	3.7	0.052

The remaining polymeric material had a number average molecular weight of 2,000 as determined by VPO in chloroform. Elemental analysis of this material gave the following results:

Found: C, 56.31; H, 4.70; N, 15.71; P, 23.08

Calc'd from Mass Spec.: C, 54.95; N, 14.79

The empirical formula calculated from the analysis is $C_{24.8}H_{24.8}N_{6.4}P_4$, for which the $\emptyset/CH_3$ ratio is 5.0/1.

Apparently $[\emptyset PN(NHCH_3)]_4$ does not undergo a simple elimination of methylamine during thermal polymerization. The presence of dimethylamine and trimethylamine and ammonia would suggest a rather complex mode of amine elimination leading to products which could not readily be characterized.

2. Reaction of $[\emptyset PN(NHCH_3)]_4$ with $[\emptyset PNCl]_4$ in Pyridine

In another attempt to prepare a polymer bridged by NCH_3 groups, a solution of equimolar amounts of β-trans-$[\emptyset PN(NHCH_3)]_4$ and β-trans-$[\emptyset PNCl]_4$ in pyridine was refluxed for seventy-two hours, after which the mixture was distilled at reduced pressure. Pyridine hydrochloride was recovered by vacuum sublimation of the residue. Twenty-five percent of the available chlorine was thus recoverd as pyridine hydrochloride. The remaining residue was readily taken up in chloroform and fractionally reprecipitated with n-hexane. An infrared spectrum of this material is shown in Figure 1. The number average molecular weight was determined as 1,330 by VPO in $CHCl_3$.

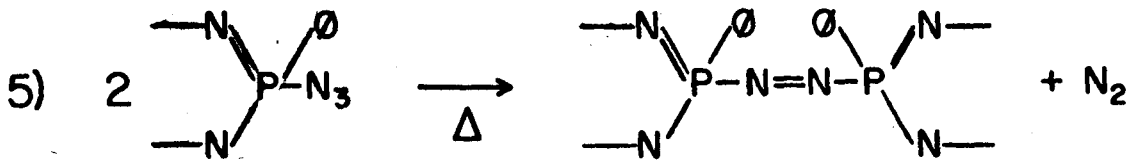
3. Polymerization of $[\emptyset PN(NHCH_3)]_4$ in Presence of BF_3

In an attempt to polymerize the tetrakismethylamide under milder conditions, the tetramer was treated with BF_3 to form an adduct which upon heating in a suitable solvent might eliminate $CH_3NH_2{:}BF_3$. The reaction was carried out in chlorobenzene at 100°C. for 24 hours. However, upon working up the resultant mixture no evidence was found for the formation of an amine boron trifluoride adduct. The reaction was repeated at 131° with the same negative result. This approach therefore was abandoned.

D. Thermal Polymerization of β-trans-$[\emptyset PN(N_3)]_4$

The behavior of the β-trans tetraazidotetraphenylphosphonitrile upon heating indicates that polymerization might be possible if azo bonds form intermolecularly as nitrogen is evolved. Data for azidophosphonitrile decompositions were recently reported by Shorts et al.[7]

Heating β-trans-$[\emptyset PN(N_3)]_4$ above its melting point, 134-5°, causes the slow evolution of a gas that is presumed to be nitrogen. This evolution becomes rapid if the melt is heated to 200°C. The product is a highly colored resinous material. Heating at 220° for fifteen minutes caused the evolution of 90% of the available nitrogen as based on the following reaction:

5) 

The product, however, was not soluble in chloroform or toluene.

E. Metal-Containing Polymers of β-trans-$[\emptyset PN(NH_2)]_4$

1. Copper-Containing Polymers

During the thermal polymerization studies with β-trans-$[\emptyset PN(NH_2)]_4$ and β-trans-$[\emptyset PN(NHMe)]_4$ it became apparent that the condensation reactions cannot have a high degree of steric control. That is, although the objective is the formation of a polymer with a highly organized geometric pattern, the very nature of a thermally induced deammonalysis can lead to irregular polymer growth. In an effort to increase the stereospecificity of this reaction, an attempt was made to conduct the elimination of ammonia on a surface. The system chosen for this work was a solid metallic salt, $CuSO_4$, suspended in an organic solution of the cyclic phosphonitrilic tetramer. The copper salt was chosen for two reasons. First, the cupric ion would act as a Lewis Acid, thereby catalyzing the elimination of ammonia. Secondly, this ion could also be expected to act as a receiver for evolved ammonia molecules, since the formation of tetraamine cupric ion is a well known reaction. The results of this initial work were not at all as expected. Rather than forming stericly oriented ladder polymers and tetraaminocupric sulfate, a polymer containing both phosphonitrilic tetramer units and copper salt was formed.

The initial experiment was conducted with a chlorobenzene solution of β-trans-$[\emptyset PN(NH_2)]_4$ and $CuSO_4.H_2O$. The copper salt was present in 100% stoichiometric excess and the two-phase mixture was stirred at 130°C for forty-eight hours. Ninety percent of the starting material was recovered, but the remaining 10% appeared as a chloroform-soluble, green-colored material. The

infrared spectrum, Figure 9, indicates that this material has a structure that is closely related to the polymers from β-trans-$[\phi PN(NH_2)]_4$.

Reactions conducted in the absence of solvent produced low molecular weight polymers. A mixture of the tetraamide and $CuSO_4,H_2O$ in a ratio of 1:1.8 was heated at 220°C for sixteen hours. A polymer with an average molecular weight of 4720 was recovered from a chloroform extract of the product. Figure 10 shows the strong absorption at 900 cm^{-1} that is typical of polymers derived from the tetraamide. Elemental analysis, given below, indicates that there is approximately one Cu^{++} ion for five tetramer units.

Found: C, 51.9; H, 4.14; N, 12.64; P, 21.72; Cu, 2.12.

Because the analysis does not add up to 100%, even including $SO_4.H_2O$, the product may have been partially hydrolyzed.

The thermal deammoniation in the presence of Cu^{++} ion was repeated with a molar ratio of $CuSO_4.H_2O$ to cyclic phosphonitrile of 4 to 1. The product, obtained after heating for six hours at 240°C, contained a chloroform soluble fraction (20% yield) that had an average molecular weight of 3600 and composition of one Cu^{++} ion for each two tretramer units.

Found: C, 50.16; H, 3.81; N, 11.63; P, 21.57; Cu, 5.02.

Subsequent experiments with thermal deammoniation in the presence of $CuSO_4.H_2O$ indicated that the NH_3 evolution starts at a temperature of 180°C as compared with a temperature of 210°C for NH_3 evolution from β-trans-$[\phi PN(NH_2]_4$ alone. However, the NH_3 evolution is only 37% complete after six days at 200°C and with a slow condensation of this type, the polymeric product is completely insoluble in chloroform.

A study of the optimum conditions for the preparation of phosphonitrile-copper salt coordination polymers was undertaken. Included in this study were the type of copper salt, the solvent, the temperature of preparation, and molar ratio of copper salt to phosphonitrilic tetramer. A summary of this study is presented in Table V.

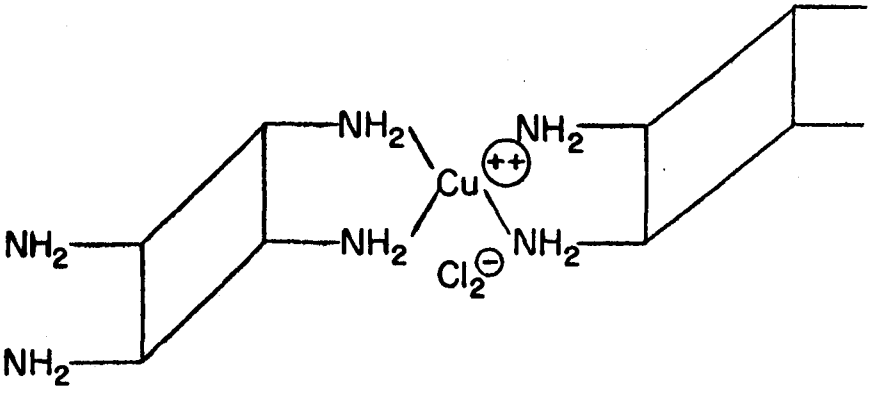
TABLE V

Preparation of β-trans-$[\phi PN(NH_2)]_4$-Copper Salt Polymeric Complexes

Copper Compound	Ratio Salt: PN Tetramer	Solvent	% Yield $CHCl_3$ Sol. Polym.	Empirical Formula of Polymer
$CuSO_4.H_2O$	10:1	CH_2Cl_2	0	--
$CuSO_4.H_2O$	1:1	THF	0	--
$CuSO_4.H_2O$	1:1	Glyme	70	--
$CuSO_4.H_2O$	1:1	CH_3CN	80	$P_4N_6C_{30}H_{29}(CuSO_4.H_2O)_{0.4}$
$CuSO_4$	1:1	CH_3CN	<15	$P_4N_6C_{30}H_{29}(CuSO_4,H_2O)$
$CuCl_2$	1:1	CH_3CN	86	$P_4N_7C_{24}H_{28}(CuCl_2).6$
$CuSO_4$	1:1	THF	0	--
$CuSO_4$	1:1	Glyme	50	$P_4N_8C_{29}H_{28}(CuSO_4).3$
$CuSO_4.5H_2O$	10:1	C_6H_5Cl	0	--
$CuCl_2$	1:1	THF	90	$P_4N_8C_{26}H_{28}(CuCl_2)_1$
$CuCl_2$	1:1	THF	96	$P_4N_{7.6}C_{26}H_{35}(CuCl_2)_1$
$CuCl_2$	1:1	Glyme	70	$P_4N_5C_{21}H_{24}(CuCl_2).75$

The optimum solvents appear to be tetrahydrofuran with cupric chloride and acetonitrile with copper sulfate monohydrate.

In order to determine how the copper salt was incorporated in the polymer, a number of experiments were conducted to find the conditions necessary for the removal of the copper. Treating the polymer with water had no effect, but agitation with 0.01N HCl caused the polymer to slowly lose the copper salt, leaving impure, but easily identified β-trans-$[\phi PN(NH_2)]_4$. Treatment of the polymer with aqueous 1.0N NaOH did not cause loss of the copper salt. Three sequestering agents, the trisodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$, the disodium salt of iminodiacetic acid, $HN(CH_2COONa)_2$, and the disodium salt of ethylenediamine tetraacetic acid were used in studies of the removal of copper salts from the polymer. In each case removal of the copper salt was rapid and the remaining material was impure β-trans-$[\phi PN(NH_2)]_4$. It is apparent that the polymer was of the following type:



The phosphonitrilic tetramer-copper salt polymeric complexes could be thermally deammoniated by heating above 180°C. The high-temperature performance of these polymers was measured with an Aminco Thermo-Grav 4.4430. One-tenth gram samples were heated at a rate of six degrees per minute in an anhydrous nitrogen atmosphere. Figure 11 shows the behavior of the polymer obtained from the thermal deammoniation of β-trans-$[\phi PN(NH_2)]_4$. The weight loss below 400°C is probably caused by the loss of additional ammonia, but above 400°C the loss of weight is primarily due to the formation of benzene via phenyl-phosphorus bond cleavage. The rate of weight loss diminishes significantly after about half the phenyl groups have been lost. The mechanism of the benzene elimination has not been established. Figure 12 shows the behavior of a polymer containing one cupric chloride per tetramer unit. Because the polymer had not been deammoniated, the initial ammonia loss was greater. Above 400°C, the loss of phenyl groups plus a small amount of NH_4Cl accounts for the 40% weight loss observed between 350°C and 800°C. Figure 13 is the thermogram of a similar polymer that had been deammoniated by heating in refluxing anisole. Obviously the first significant weight losses are due to loss of benzene. Figure 14 shows the behavior of a complex with the formula $[\phi PN(NH_2)]_4.CuSO_4.H_2O$. The first losses are from NH_3 and H_2O. Note that the losses from phosphorus-phenyl cleavage occur at a significantly higher temperature.

A detailed study of the deammoniation of β-trans-$[\phi PN(NH_2)]_4$. $CuCl_2$ was not made, but the polymeric residue was soluble in chloroform and retained the green color of the polymer containing four amino groups per cyclic tetramer. The infrared pattern of this material, Figure 15, shows a new absorption band at 1150 cm^{-1}. This absorption is typical of phosphonitrilic cyclics that have a metal coordinated with the ring nitrogens. Treatment of the deammoniated polymer with ethylenediaminetetraacetic acid, disodium salt, did not lead to the rapid removal of copper salts as had been observed with the tetramer-Cu salt polymer complex. These observations led to the conclusion that the deammoniated polymers contain copper ions partially bound to the ring nitrogens, and more tightly held than the cupric ions associated with four amino groups.

2. Cobalt-Containing Polymers

Because copper salts with a coordination number of four could be incorporated into the polymers, it was of interest to attempt the preparation of polymers containing a metallic ion with a coordination number of six.

Anhydrous cobaltous chloride, $CoCl_2$, was prepared by heating $CoCl_2.6H_2O$ for six hours at 130°C in an HCl atmosphere. In the first preparation of this type, an equimolar mixture of $CoCl_2$ and β-trans-$[\phi PN(NH_2)]_4$ was heated for seven hours at 210-240°C. During this period, 74% of the theoretical amount of NH_3 ($2NH_3$ molecules per cyclic tetramer) was evolved. The product, a bright-blue chloroform soluble material, was obtained in 75% yield. Elemental analysis was consistent with an empirical formula of $[\phi_4P_4N_4(NH)_{1.5}(CoCl_2).{}_{23}(HOH)_2]_n$, i.e.,

Found: C, 50.82; H, 4.22; N, 12.76; P, 21.46; Cl, 3.23.

A subsequent preparation led to the observation that not only NH_3 was evolved, but rigorous heating caused NH_4Cl to be formed as well. This implied that chlorine from the $CoCl_2$ participated in the condensation reactions. When heated to 250°C, a polymeric material from equimolar amounts of β-trans-$[\phi PN(NH_2)]_4$ and $CoCl_2$ gave a product with an empirical formula of approximately $\phi_4P_4N_4(OH)_4(CoClOH)_{1.4}$, i.e.,

Found: C, 39.4; H, 4.4; N, 8.4; Co, 12.0.

When the cobalt containing polymer was prepared in acetonitrile, an 85% yield of product that had not lost ammonia or ammonium chloride was obtained. The empirical formula $[(\phi PNNH_2)_4.CoCl_2]n$ is consistent with the elemental analysis.

Found: C, 41.30; H, 4.92; N, 15.73; Cl, 12.59; P, 17.69; Co, 8.05.

The infrared spectrum of this polymeric adduct is shown in Figure 16. This spectrum is similar to those of the polymers from β-trans-$[\phi PN(NH_2)]_4$, but very different from the spectrum of a cobalt-PN polymer prepared in the melt (Figure 17). It is apparent from the difference in these spectra that in the polymer prepared at higher temperatures, cobalt is coordinated with the ring nitrogens, whereas in the polymer prepared in acetonitrile, the cobalt is coordinated with the amino groups and not the nitrogens in the ring.

Thermograms obtained for the cobalt-containing complexes indicate a steady loss of ammonia up to about 400°C and then an additional loss of benzene and NH_4Cl (see Figure 19). This polymer is not as thermally stable as the polymer obtained from β-trans-$[\phi PN(NH_2)]_4$ with no associated metal.

Larger preparations of the cobaltous chloride-phosphonitrile polymer were made for studies of the polymer properties. In these studies it was established that the cobalt salts can be readily removed from the one-to-one adduct of $CoCl_2$ and β-trans-$[\phi PN(NH_2)]_4$ by the use of a sequestering agent, trisodio-nitrilotriacetic acid, $[N(CH_2COONa)_3]$. If this polymer is heated, ammonia evolution leads to a polymer with an elemental analysis as follows:

Found: P, 19.6; H, 13.3; C, 43.3; H, 3.8; Cl, 9.8; Co, 8.3.

This is consistent with an empirical formula of $[\phi PN(NH)_{\frac{1}{2}}]_4.CoCl_2$. This deammoniated polymer does not readily react with the sequestering agent.

3. Miscellaneous Metal-Containing Polymers

(a) Nickel-Containing Polymer

One preparation of a polymer from β-trans-$[\phi PN(NH_2)]_4$ and $NiCl_2$ was conducted at an elevated temperature without solvent. As in the case of the cobalt polymers prepared in the melt, the composition indicated

Found: C, 47.8; H, 4.4; N, 9.3; P, 20.2; Cl, 0.7; Ni, 3.2

that the polymer did not contain amino groups but probably had oxygen or hydroxy groups as the linking groups between phosphonitrile rings.

A subsequent preparation was conducted with equimolar amounts of $NiCl_2$ and β-trans-$[\phi PN(NH_2)]_4$ in acetonitrile. The polymeric product from this reaction was a yellow-green solid with an empirical formula of $(C_6H_5)_4P_4N_4(NH_2)_4(NiCl_2)\cdot_5(H_2O)_{1\cdot5}$

Found: C, 43.05; H, 4.74; N, 15.92; P, 18.66; Ni, 4.60; Cl, 10.12.

No further work has been done with the nickel-phosphonitrile polymers.

(b) Iron-Containing Polymer

By gently refluxing a mixture of β-trans-$[\phi PN(NH_2)]_4$ and $FeCl_2$ in acetonitrile, a 90% yield of material presumed to be $\left([\phi PN(NH_2)]_4.FeCl_2\right)_n$ was prepared.

Found: C, 42.5; H, 4.9; N, 16.3; P, 17.5; Fe, 8.6; Cl, 10.4.

This polymer melts at 96°C and when heated above 110°C, evolves ammonia. The infrared spectrum, Figure 18, is essentially the same as those of other metal-phosphonitrile polymers.

(c) Silver-Containing Polymer

A reaction tube containing β-trans-$[\phi PN(NH_2)]_4$ and AgCl in a molar ratio of 1:2 was heated to 230°C for seven hours. During this period ammonia was evolved and an insoluble grey solid was formed. Elemental analysis:

Found: C, 22.77; H, 2.05; N, 7.63; P, 12.05; Cl, 12.09

indicated it had an empirical formula of $\phi_4P_4N_4(NH)_{1\cdot5}(OH)\cdot_5(AgCl)_{3\cdot5}$.

II. $[CH_3PN(NH_2)]_{3,4}$

A. Preparation

Non-geminal methylaminophosphonitriles can be prepared by the following sequence of reactions.[1]

1. $CH_3PCl_2 + Cl_2 \rightarrow CH_3PCl_4$
2. $xCH_3PCl_4 + xNH_4Cl \rightarrow [CH_3PNCl]_x + 4xHCl$
3. $[CH_3PNCl]_x + 2xNH_3 \rightarrow [CH_3PN(NH_2)]_x + NH_4Cl$

The yield of methylphosphonitrile obtained from reaction (2) is poor, approximately 20-30 percent. Yields of pure product are further reduced during the work-up since $[CH_3PNCl]$ appears to be hydrolytically unstable. For this reason the crude product was reacted with anhydrous ammonia to form the amide. The amide was separated from by-product ammonium chloride by extraction with acetonitrile. An infrared spectrum of the crude amide is shown in Figure 7. The weak absorption at 2650 cm^{-1} (due to POH) indicates that some hydrolysis has occurred.

B. Polymerization

Thermal deammoniation of the amide takes place above 150°C and is essentially complete at about 400°C. A TGA of the amide is shown in Figure 8. At temperatures above 400°C, degradation occurs. The principal volatile degradation product is ethylene which was identified by mass spectroscopy.

Based on the above results, namely (1) hydrolytic instability of both $[CH_3PNCl]_4$ and $[CH_3PN(NH_2)]_4$ which would make isolating and characterizing isomers of $[CH_3PNCl]_4$ exceedingly difficult and, (2) the thermal instability of polymeric methyl phosphonitrile, a decision was made to suspend further work on this system.

EXPERIMENTAL

I. Reactions of $[\emptyset PNCl]_4$

A. Preparation of $[\emptyset PN(NH_2)]_4$

In a typical synthesis fifty grams of β-trans-$[\emptyset PNCl]_4$ was partially dissolved in 300 ml. of THF. Ammonia gas was passed through the solution at room temperature. After several hours the solution was filtered while hot to remove ammonium chloride. More ammonia was added to the filtrate but no precipitate formed. The reaction, therefore, was assumed to be complete. Tetrakisamide was recovered by considerably reducing the volume of solution at reflux and allowing a precipitate to form while cooling. The reaction was repeated four times and, in each case, the yield of β-trans-$[\emptyset PN(NH_2)]_4$, m.p. 222-4°, exceeded 75%.

B. β-trans-$[\emptyset PN(N_3)]_4$

A mixture containing β-trans-$[\emptyset PNCl]_4$, (25 g., 0.0397 mole) and sodium azide, (45 g. 0.70 mole) was placed in 250 ml. of acetonitrile. All of the phosphonitrile and some of the azide dissolved. The reaction mixture was heated to 80°C. and held at this temperature for four hours. The excess azide and by-produced sodium chloride were removed by filtration. Product was recovered by distilling off the solvent. A recrystallization from chloroform gave 23 g. of β-trans-$[\emptyset PNN_3]_4$ m.p. 134-5°C. for a yield of 87%.

C. β-trans-$[\emptyset PN(NCS)]_4$

A solution containing β-trans-$[\emptyset PNCl]_4$, (3 g., 4.76 moles) and potassium thiocyanate (1.85 g., 19.0 mmoles) in 25 ml. of anhydrous acetonitrile was heated to 80° in a nitrogen atmosphere. The temperature was maintained at 80° for four hours. After cooling, by-produced KCl was filtered and the filtrate was concentrated by evaporating most of the solvent. The crystallized product, m.p. 145-7°C., weighed 3.0 g. for a yield of 88%.

D. β-trans-$[\emptyset PN(NHCH_3)]_4$

Gaseous methylamine was passed through a solution of β-trans-$[\emptyset PNCl]_4$ (115 g., 0.183 mole) in one liter of dry tetrahydrofuran. The precipitated methylamine hydrochloride that formed was removed by filtration and the proeess then repeated to insure that all tetrachlorophosphonitrile had been converted to the tetraamide. The solution was concentrated and 54 g. or .089 mole of β-trans-$[\emptyset PN(NHCH_3)]_4$ was recovered for a yield of 48.4% m.p. 151-2°C.

E. Reaction with Formaldehyde

In methanol, 3.6 mmoles of $[\emptyset PN(NH_2)]_4$ was treated with an excess of aqueous formaldehyde in the presence of two drops of pyridine. The mixture was refluxed for 48 hours during which time a precipitate formed. The precipitate, 1.0 g. was recovered by filtration.

II. Polymers of $[\emptyset PN(NH_2)]_4$

A. Thermal Deammoniation of β-trans-$[\emptyset PN(NH_2)]_4$

The cyclic tetramer was polymerized by heating small samples, 1-5 g., in a dry nitrogen atmosphere. Samples were heated in an oil bath. Temperatures were maintained to ± 1°C. with a controller. The evolved ammonia was dissolved in water and titrated with standard acid. After the polymerization was complete, the polymer was stirred with 75 ml. of anhydrous chloroform for twelve hours. The portion that dissolved was considered a useful polymer and molecular weights were obtained for this material.

By redissolving the polymer in chloroform and precipitating approximately one fifth of the solid with n-heptane, highest molecular weight fractions were obtained.

B. Reaction with Toluene-2,4-Diisocyanate

To two grams of the tetraamide in xylene was added 2 molar equivalents of the diisocyanate. A precipitate formed during the addition which, after filtration, proved to be an insoluble solid that did not melt at 300°C. No other product was recovered from this reaction.

C. Copolymerization of β-trans-$[\emptyset PNCl]_4$ and β-trans-$[\emptyset PN(NH_2)]_4$

A solution containing β-trans-$[\emptyset PNCl]_4$, 7.87 g., 0.0125 mole, β-trans-$[\emptyset PN(NH_2)]_4$, 6.90 g., 0.0125 mole, and 3.85 g., 0.05 mole, of pyridine in 200 ml. of dry chlorobenzene was heated at reflux temperature (130°C.) for twenty-four hours. A product, identified as pyridine hydrochloride by its infrared spectrum was removed by filtration and a polymeric product was obtained upon concentrating the reaction mixture.

D. Copolymer of β-trans-$[\emptyset PN(NH_2)]_4$ and Pyromellitic Tetraacid Chloride

Pyromellitic tetraacid chloride was obtained from Eastman DPI. To a flask containing 2.2 g. (7.26 moles) of the acid chloride was added 2.3 g. of pyridine in 50 ml. of anhydrous chloroform. Upon addition of the pyridine the solution turned deep red.

The solution was brought to reflux at about 64°C. and a chloroform solution of β-trans-$[\emptyset PN(NH_2)]_4$, 4.0 g. (7.26 moles) was slowly added. After several hours a precipitate formed. The solution was filtered hot after 24 hours. A grey precipitate, 3.35 g., which softened at 230°C., was recovered. No other material suitable for characterization was recovered.

E. Copolymerization of $[\emptyset PN(NH_2)]_4$ and Pyromellitic Dianhydride (PMDA)

A solution containing 4.0 g. (7.25 mmoles) of β-trans-$[\emptyset PN(NH_2)]_4$ and 1.585 g. (7.25 mmoles) of PMDA in 35 ml. of dimethylformamide was heated. At 80°C. the solution turned yellow and at 100°C. a precipitate formed while the solution turned green. Reflux began at about 135°. A distillation head

was attached to the reaction flask and some distillate removed until refluxing proceeded at 152°C.

After 1 hour the solution was cooled and filtered. A small amount of grey solid, less than 0.1 g., was removed. This solid did not melt until 300°. The filtrate was evaporated to dryness at reduced pressure of 10 mm. and 60°C. A deep brown glassy solid remained which had a softening temperature of approximately 70°C. The residue, 5.44 g., was taken up in 200 ml. of hot chloroform and filtered. Of the total sample 1.55 g. remained insoluble. This sample was sent for analysis.

The chloroform filtrate volume was reduced to about 5 ml. and n-heptane was added whereupon an oil separated. This oil was washed several times with chloroform-n-heptane and then dried under a high vacuum. The oil solidified to a brown solid.

In another experiment two grams of tetraamide was treated with an equivalent amount of PMDA. Reaction at the reflux temperature of DMF was conducted by slowly adding one of the reagents to the other while distilling off a mixture of by-produced water and DMF. After refluxing for several hours the solution was filtered and the filtrate evaporated to dryness at reduced pressure. The black residue obtained in this way was insoluble in all organic solvents tried.

For the reaction carried out at room temperature no attempt was made to remove the water that formed. Contrary to the previous experiments the solution did not turn deep brown. Upon evaporation of DMF at reduced pressure a solid was obtained. The solid was only partially soluble in chloroform. Elemental analyses are given in the Discussion Section.

III. Polymers of $[\text{ØPN(NHCH}_3)]_4$

A. Thermal Polymerization of β-trans-$[\text{ØPN(NHCH}_3)]_4$

This material was polymerized by heating the tetramer under a nitrogen atmosphere in a small furnace fitted with a temperature controller. As in the case of the $[\text{ØPN(NH}_2)]_4$ the evolved amine was measured by titrating with standard acid. In a typical run, a three gram sample was heated to 300°C. and during an eleven hour period, 0.26 g. or 85% of the theoretically available amine was evolved. The product was dissolved in chloroform, and a molecular weight obtained.

B. Reaction of $[\text{ØPN(NHCH}_3)]_4$ with $[\text{ØPNCl}]_4$ in Pyridine

A solution of 3 g. (4.93 mmoles) of $[\text{ØPN(NHCH}_3)]_4$ and 2.62 g. (4.93 mmoles) of $[\text{ØPNCl}]_4$ in 50 ml. of anhydrous pyridine was brought to reflux at 115°C. After 72 hours the solvent was removed by distillation at reduced pressure. The residue was then transferred to a sublimation apparatus and at 175° and 0.010 Torr a sublimate was collected. The sublimate was dissolved in water and analyzed for chloride. Five mmoles of chloride were found as AgCl.

The remaining residue was taken up in 10 ml. of chloroform and upon addition of pentane an oil separated which, when triturated, turned to a solid. Molecular weight of this solid is 1,330 as determined by VPO in chloroform.

C. Attempted Polymerization of $[\emptyset PN(NHCH_3)]_4$ in the Presence of BF_3

Two grams (3.29 mmoles) of $[\emptyset PN(NHCH_3)]_4$ and 6.58 mmoles of $BF_3.Et_2O$ in chlorobenzene was kept at 100°C. for 24 hours. Only a slight haziness developed during this time. Upon evaporation of the solvent only starting material was recovered.

The reaction was repeated at 131°C. with the same negative results.

IV. Thermal Polymerization of $[\emptyset PN(N_3)]_4$

The tetraazide was heated under nitrogen in the same apparatus used for the thermal polymerization of β-trans-$[\emptyset PN(NH_2)]_4$. A gas burette was used to collect the N_2 that evolved upon heating the tetraazide. In a typical run, 0.3 g. of β-trans-$[\emptyset PN(N_3)]_4$ was heated to 200° for four hours. During this period, 40 ml. of N_2 (corr. to STP) or 90% of the theoretical amount, was evolved. The product, a black resinous material, was not appreciably soluble in either chloroform or toluene.

V. Metal-Containing Polymers of β-trans-$[\emptyset PN(NH_2)]_4$

A. Copper-Containing Polymers

1. Prepared with $CuSO_4.H_2O$ in Chlorobenzene

A solution containing β-trans-$[\emptyset PN(NH_2)]_4$ (2.0 g., 3.63 mmole) in 25 ml. of anhydrous chlorobenzene was combined with copper sulfate-monohydrate (1.29 g., 7.25 mmole) and this mixture was heated at 90°C for forty-eight hours. The solution developed a dark green color but all of the copper salt did not go into solution. A pale green, methylene chloride-soluble material was isolated from this reaction mixture along with about 90% of β-trans-$[\emptyset PN(NH_2)]_4$. The product had an infrared spectrum that was essentially identical with the deammoniated polymer from β-trans-$[\emptyset PN(NH_2)]_4$. Several attempts to separate copper or copper salts from this polymer by extraction or recrystallization with chloroform, chlorobenzene, methylene chloride and benzene were made, but the green color remained. Complete characterization of the product was not attained.

2. Preparation of $[\emptyset PN(NH_2)]_4$-$CuSO_4.H_2O$ Adduct Without Solvent

Copper sulfate-monohydrate (1.82 g., 1.0 mmole) and β-trans-$[\emptyset PN(NH_2)]_4$ (1.0 g., 1.81 mmoles) were heated under nitrogen and held for sixteen hours. A green-colored polymer that had a molecular weight of 4720 was obtained. Elemental analysis indicated that the polymer was partially deammoniated and partially hydrolyzed and contained approximately one copper ion for each five phosphonitrile cyclic units.

3. Deammoniation Studies of Copper-Containing Polymers

The deammoniation of β-trans-$[\phi PN(NH_2)]_4$ in the presence of copper sulfate was investigated by measuring the rate and extent of ammonia evolution while heating various mixtures of the two in a nitrogen atmosphere. In a typical experiment, β-trans-$[\phi PN(NH_2)]_4$ (3.0 g., 5.4 mmole) and $CuSO_4 \cdot H_2O$ (9.63 g., 54.5 mmole) were heated at 200°C for six days. During this period, 4.03 mmole of NH_3 was evolved, most of it during the first eight hours. The yield of chloroform soluble product was 0.35 g. or 10%.

4. Preparation in Tetrahydrofuran

The optimum process for the preparation of a polymeric 1:1 adduct was with equimolar amounts of phosphonitrile tetramer and copper salt and a solvent that dissolves at least some of the copper salt and all of the tetramer. Tetrahydrofuran, dimethoxyethane (glyme), and acetonitrile were used. A typical preparation is reported here.

A solution of β-trans-$[\phi PN(NH_2)]_4$ (5.0 g., 9.0 mmole) in 200 ml. of tetrahydrofuran (freshly distilled from $LiAlH_4$) was combined with $CuCl_2$ (1.21 g., 9.0 mmole) and this mixture was held at 65°C for 120 hours. The solution developed a dark green color during this period and essentially all the cupric chloride dissolved. The chloroform soluble product weighed 5.95 g. for a yield of 96%. The melting point was 101-110°C.

5. Experiments with Removal of Copper

A tenth of a gram of polymeric phosphonitrile-copper sulfate adduct containing 4.6% copper was dissolved in 10 ml. of chloroform and this solution was placed in a test tube containing 10 ml. of 0.1N HCl. The two-phase mixture was agitated for twenty-four hours. After this period a small amount of precipitate had formed, but both this material and the phosphonitrile that remained soluble in the chloroform had a pale green color.

A similar sample was agitated for one hour with 10 ml. of 1.0N HCl and in this case, the recovered polymer was colorless although the infrared spectra indicated that the phosphonitrile had been partially hydrolyzed.

In a third experiment a tenth gram of copper containing polymer in 10 ml. of 1.0N NaOH. No change with the polymer could be detected after twenty-four hours.

A fourth experiment was conducted with a sequestering agent. A solution of 0.1 g. of polymer in 10 ml. of chloroform was agitated with an aqueous solution containing 0.04 g. of the trisodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$. The green chloroform solution slowly turned colorless while the aqueous layer developed a pale blue-green color. The infrared spectrum of the recovered phosphonitrile was essentially that of β-trans-$[\phi PNNH_2]_4$.

B. Cobalt-Containing Polymers

1. Preparation with $CoCl_2$ Without Solvent

Anhydrous $CoCl_2$ was prepared by heating $CoCl_2.6H_2O$ to 130°C while passing a stream of HCl through the vessel. This process was continued until the weight of the material remained constant (at the theoretical weight) during a half-hour period.

A mixture of β-trans-$[\phi PN(NH_2)]_4$ (1.5 g., 2.7 mmole) and $CoCl_2$ (0.38 g., 2.7 mmole) was mixed with a mortar and pestle, then heated under nitrogen to a temperature of 240°C. During a sever-hour period, 4.06 mmole of ammonia was evolved. The product, a bright-blue solid, was soluble in dimethylformamide, tetrahydrofuran and chloroform. Elemental analysis indicated it contained one cobalt per phosphonitrilic tetramer and had a molecular weight of 5000.

2. Preparation with $CoCl_2$ in Acetonitrile

A solution containing β-trans-$[\phi PN(NH_2)]_4$ (1.5 g., 2.7 mmole) and anhydrous $CoCl_2$ (0.45 g., 2.7 mmole) in 150 ml. of anhydrous acetonitrile was heated to 80°C for sixty hours. The product, a bright-blue solid, weighed 1.7 g. for a yield of 80%. Elemental analysis and an infrared spectrum established that it was a 1:1 adduct, but the solubility in chloroform was too low to obtain a molecular weight by vapor phase osmometry.

3. Removal of Cobalt with a Sequestering Agent

A tenth gram sample of the cobalt-phosphonitrile adduct was dissolved in chloroform and this was agitated with an aqueous solution of the trisodium salt of nitrilo-triacetic acid, $N(CH_2COONa)_3$. The disappearance of the blue color in the organic layer occured in less than one hour and the water layer developed a pale-pink cast. An infrared spectrum of the recovered phosphonitrile was essentially identical with that of β-trans-$[\phi PN(NH_2)]_4$.

C. Nickel-Containing Polymers

1. Preparation with $NiCl_2$ in the Melt

A mixture of β-trans-$[\phi PN(NH_2)]_4$ (2.0 g., 3.6 mmole) and $NiCl_2$ (0.46 g., 3.6 mmole) was heated under nitrogen for ten hours at a temperature of 230°C. Ammonia evolution started when the temperature reached 200°C, and during the ten-hour period 4.1 mmoles of NH_3 was evolved. The product that was recovered from the solution was a yellow-green color, weighed 2.3 g. (90% yield) and had limited solubility in chloroform, methylene chloride, tetrahydrofuran and pyridine. Elemental analysis and an infrared spectrum were obtained.

2. Preparation with $NiCl_2$ in Acetonitrile

A solution containing β-trans-$[\phi PN(NH_2)]_4$ (1.5 g., 2.7 mmole) and $NiCl_2$ (0.35 g., 2.7 mmole) in 150 ml. of acetonitrile was stirred at

room temperature for three days. The product, a yellow-green powder, weighed 0.85 g. for a yield of 20%. This product evolved ammonia at 197°C, was soluble in ethanol, tetrahydrofuran, and dimethylformamide, and was insoluble in diethylether and benzene. Elemental analyses and infrared spectrum were obtained.

D. Iron-Containing Polymers

A solution containing β-trans-$[\emptyset PN(NH_2)]_4$ (1.5 g., 2.7 mmole) and $FeCl_2$ (0.34 g., 2.7 mmole) in 150 ml. of acetonitrile was stirred at room temperature for eighteen hours and then at 40°C for an additional twenty-four hours. The solution was filtered and evaporation of the filtrate gave 1.65 g. (89% yield) of a pale-yellow solid with an mp of 96-106°C. Elemental analyses and an infrared spectrum were obtained for this product.

E. Silver-Containing Polymers

A mixture of β-trans-$[\emptyset PN(NH_2)]_4$ (1.5 g., 2.7 mmole) and AgCl (0.8 g., 5.4 mmole) was ground to a fine powder and then heated slowly to a temperature of 232°. During a seven-hour period, 3.7 mmole of ammonia was evolved. The product, a light-grey material, weighed 1.9 g. and was infusible and insoluble in all solvents. Elemental analysis indicated it contained four silver ions per tetramer unit and was therefore highly cross-linked.

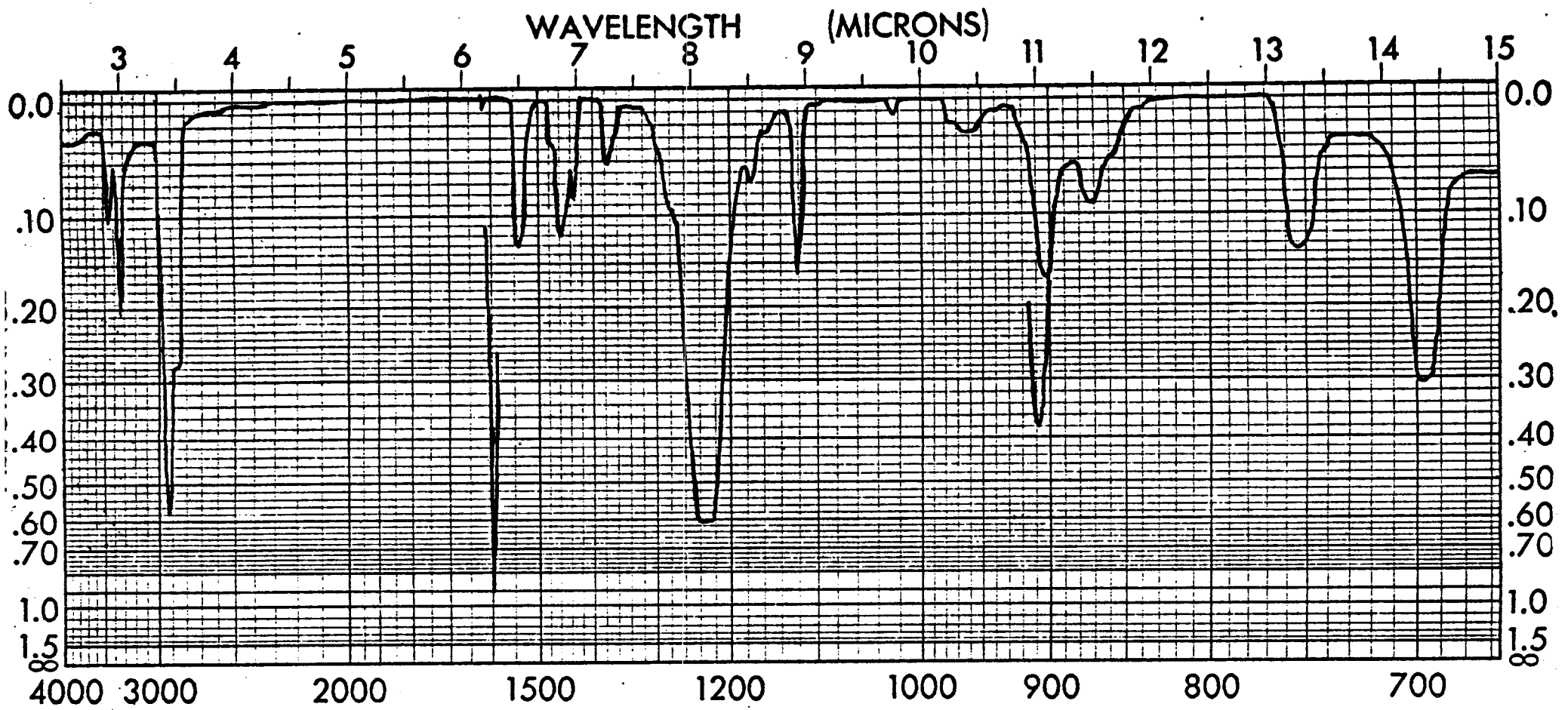


Figure 1

Infrared Spectrum of β-trans-$[\text{ØPN(NH}_2)]_4$.

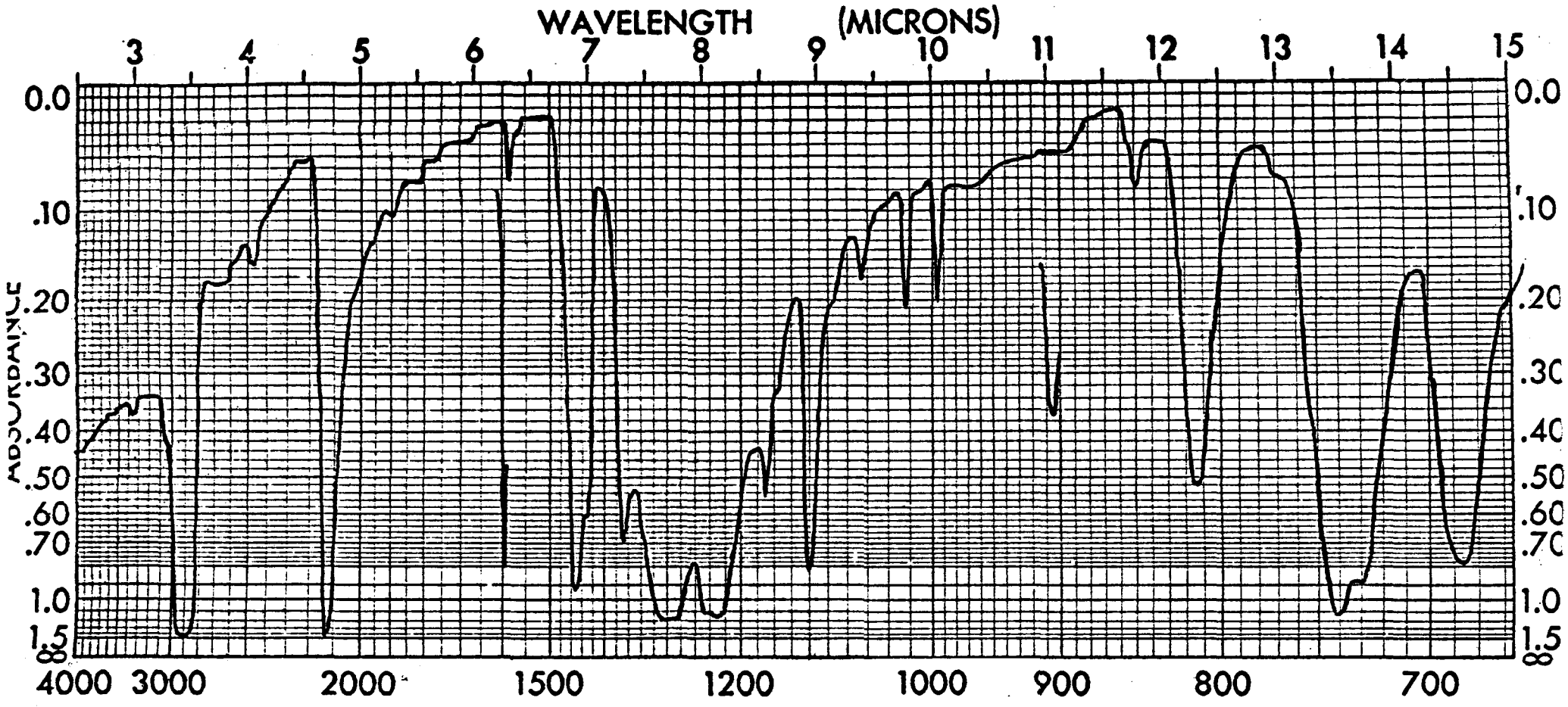


Figure 2

Infrared Spectrum of β-trans-$[\phi PN(N_3)]_4$

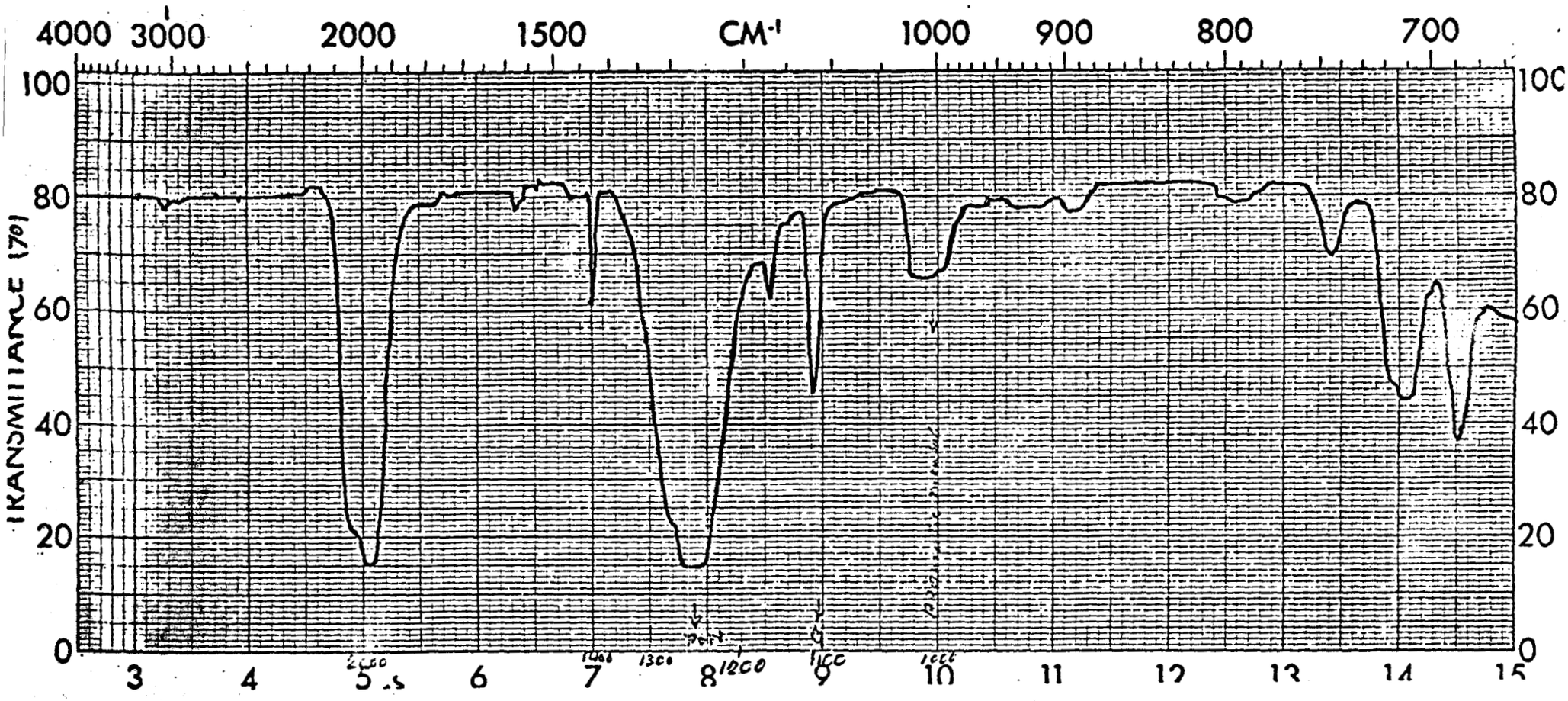


Figure 3

Infrared Spectrum of β-trans-[ØPN(NCS)]$_4$

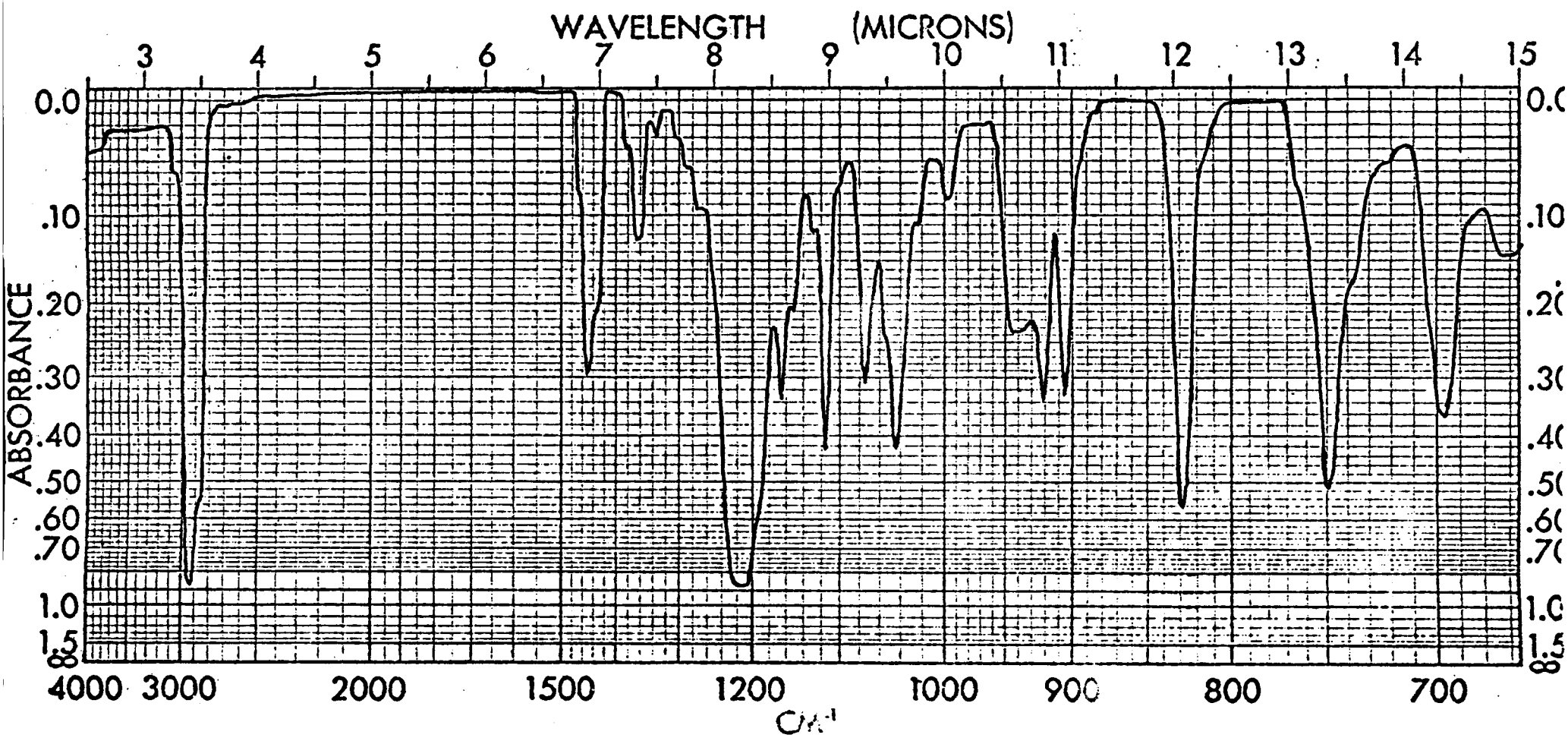


Figure 4

Infrared Spectrum of Product $[\phi PN(NH_2)]_4 + H_2CO$ in CH_3OH

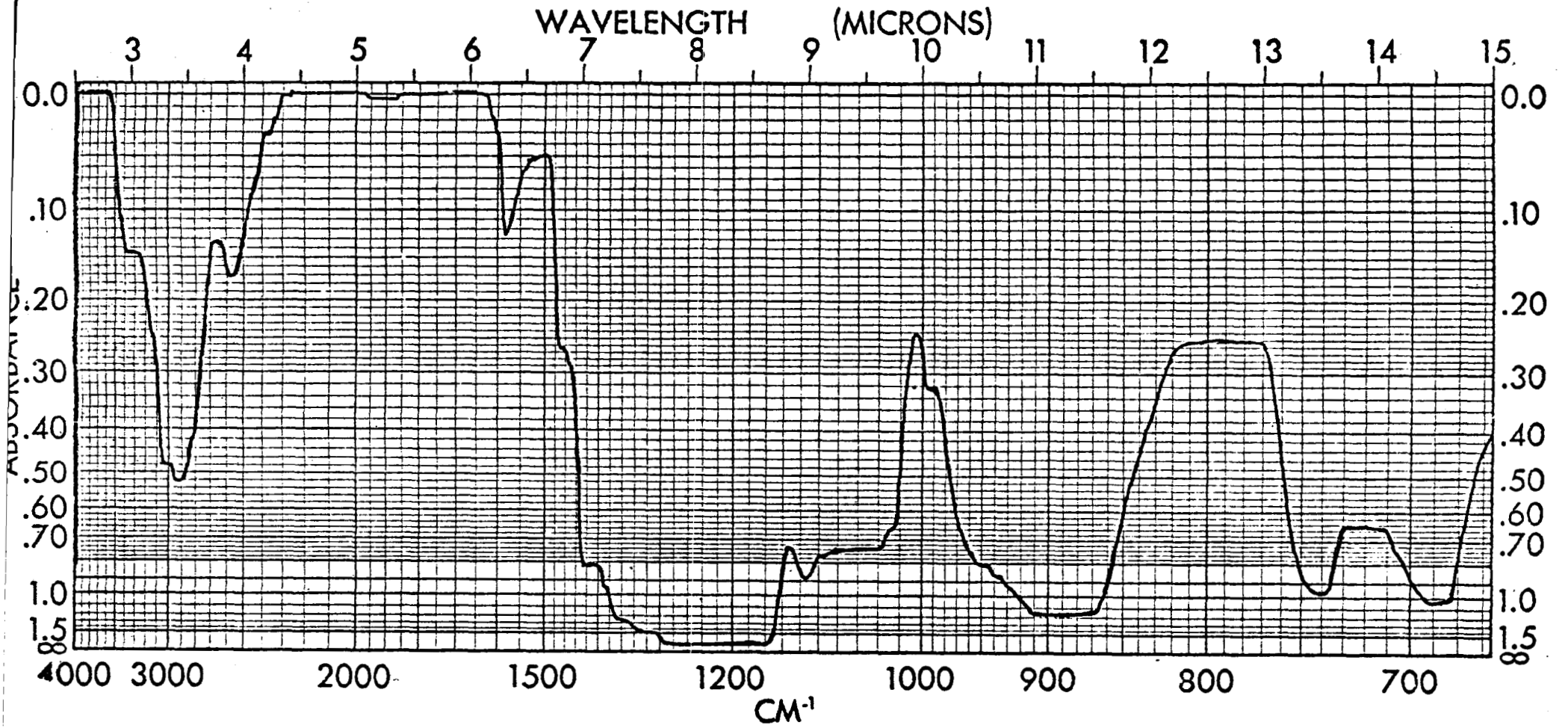


Figure 5

Infrared Spectrum of Product of Reaction $[\phi PNCl]_4 + [\phi PN(NH_2)]_4$ in CH_2Cl_2

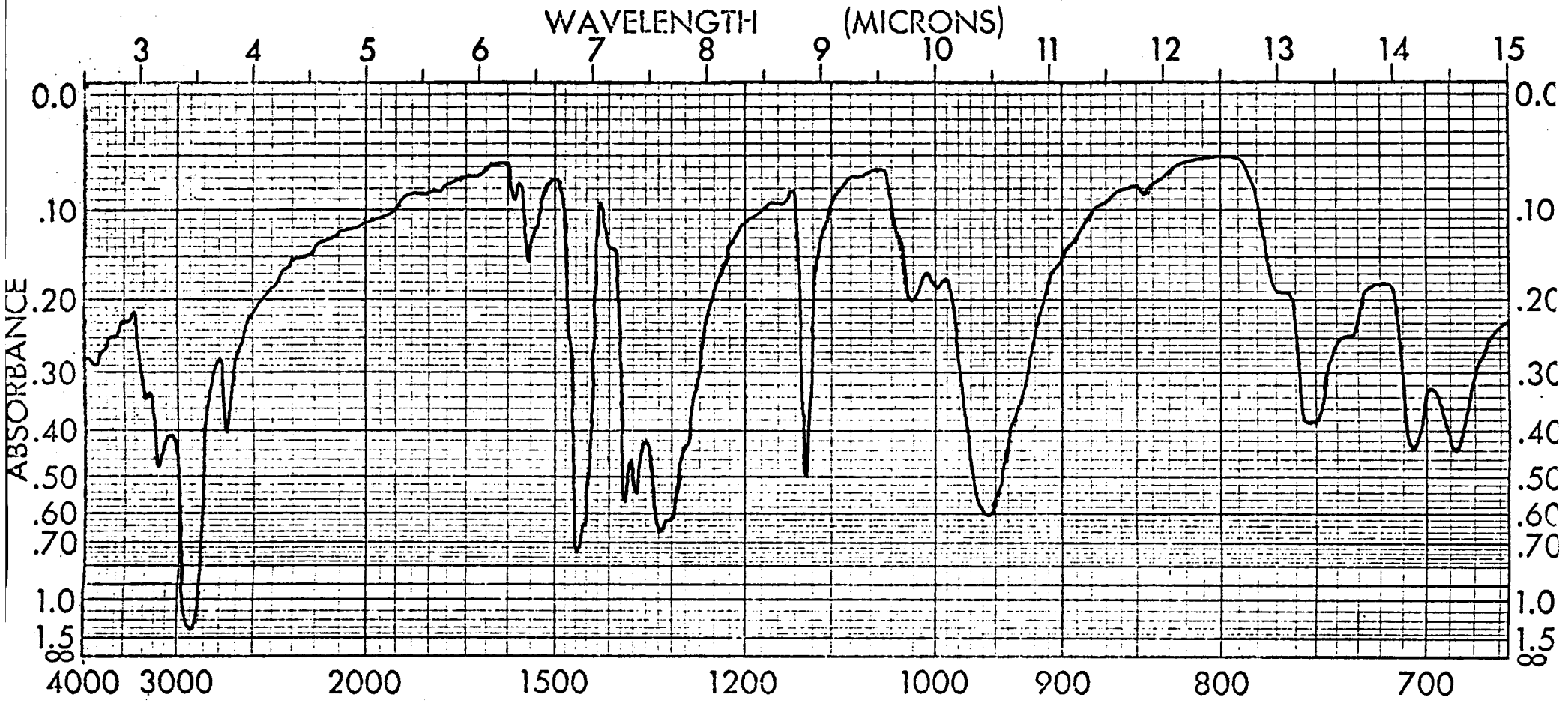


Figure 6

IR Spectrum of Product of Reaction of PMTC with β-trans-$[\phi PN(NH_2)]_4$

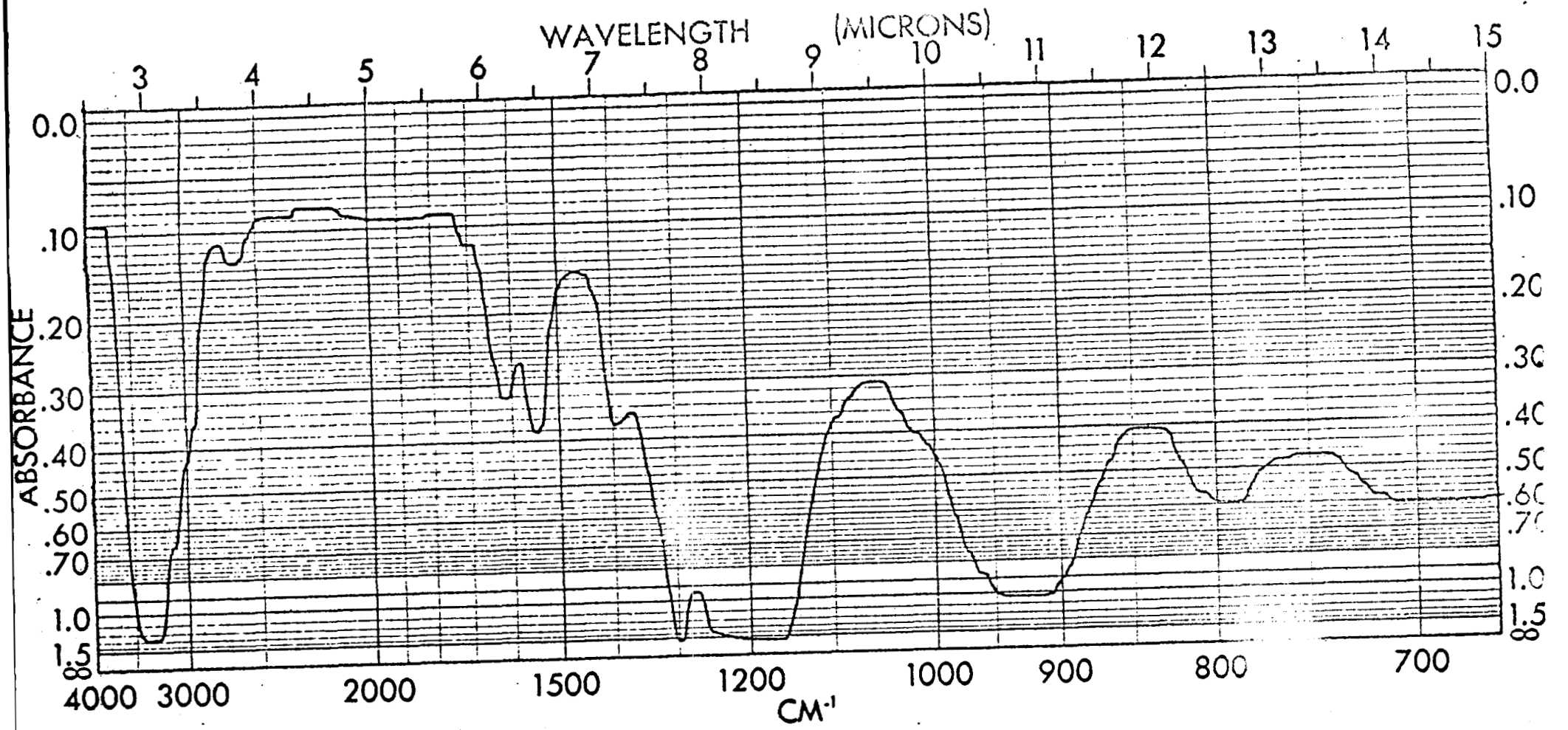


Figure 7

IR Spectrum of $[CH_3PN(NH_2)]_{3,4}$

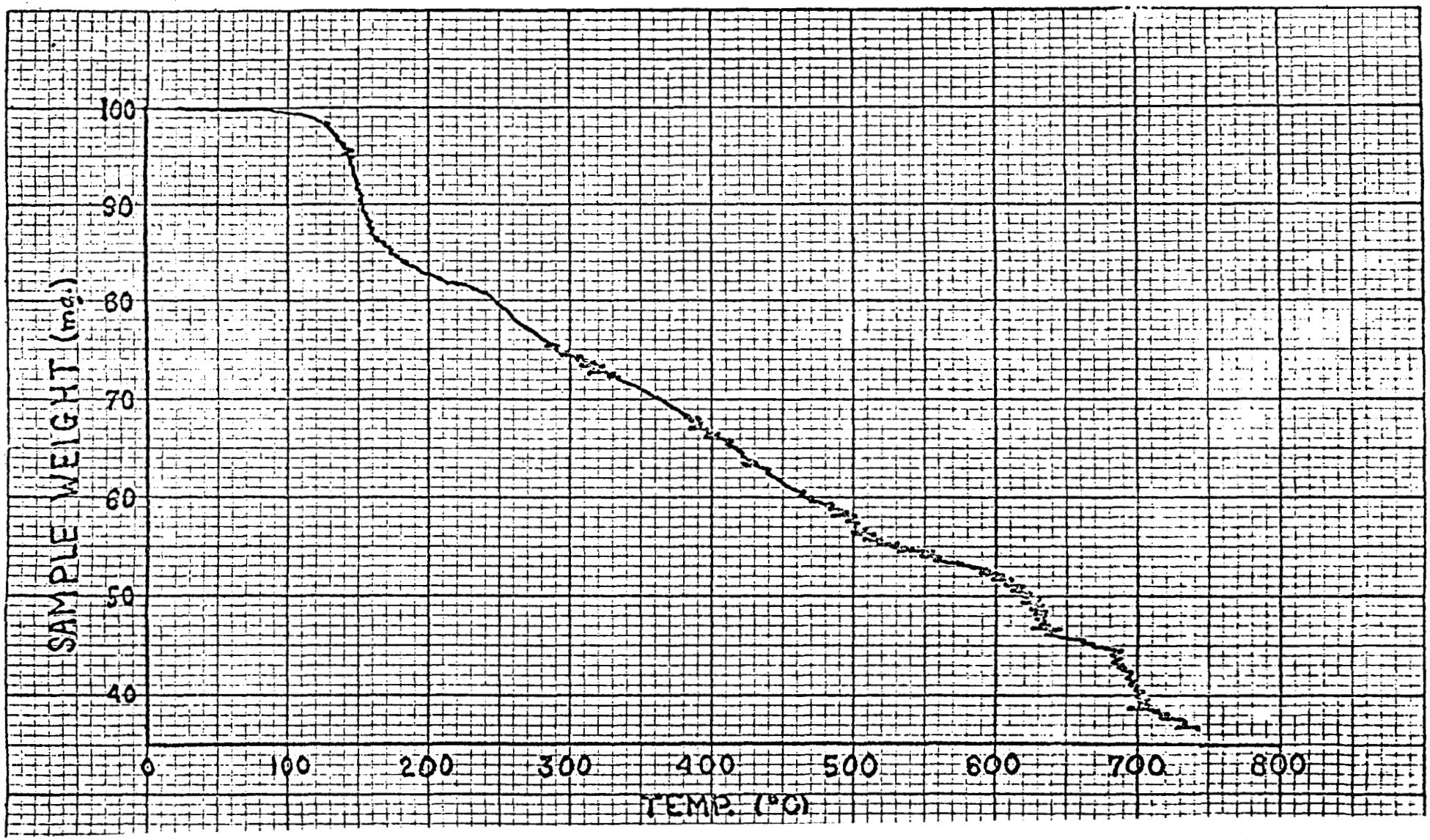


Figure 8

Thermogravimetric Analysis of $[CH_3PN(NH_2)]_4$

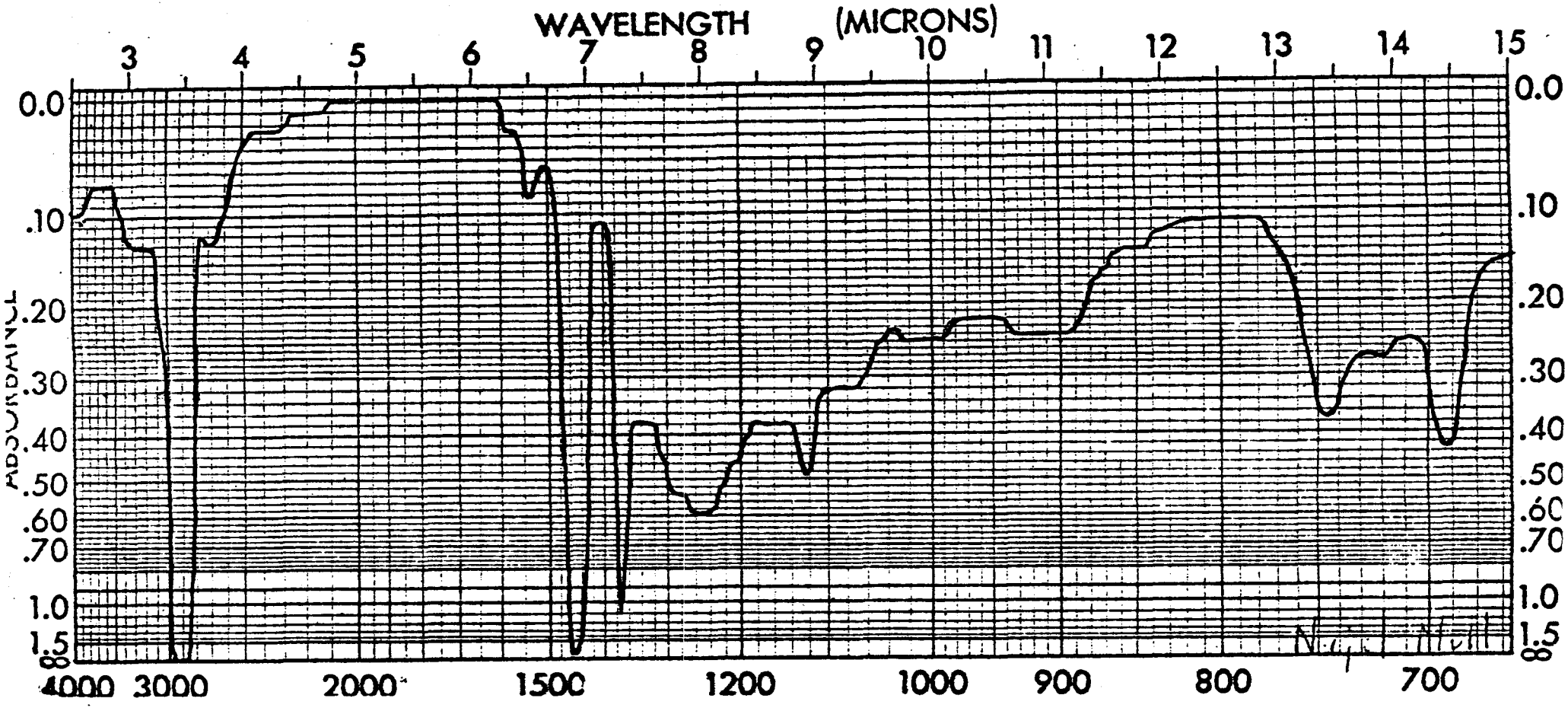


Figure 9

Infrared Spectrum of Product of Reaction β-trans-$[\phi PN(NH_2)]_4$ + $2CuSO_4.H_2O$ in Chlorobenzene

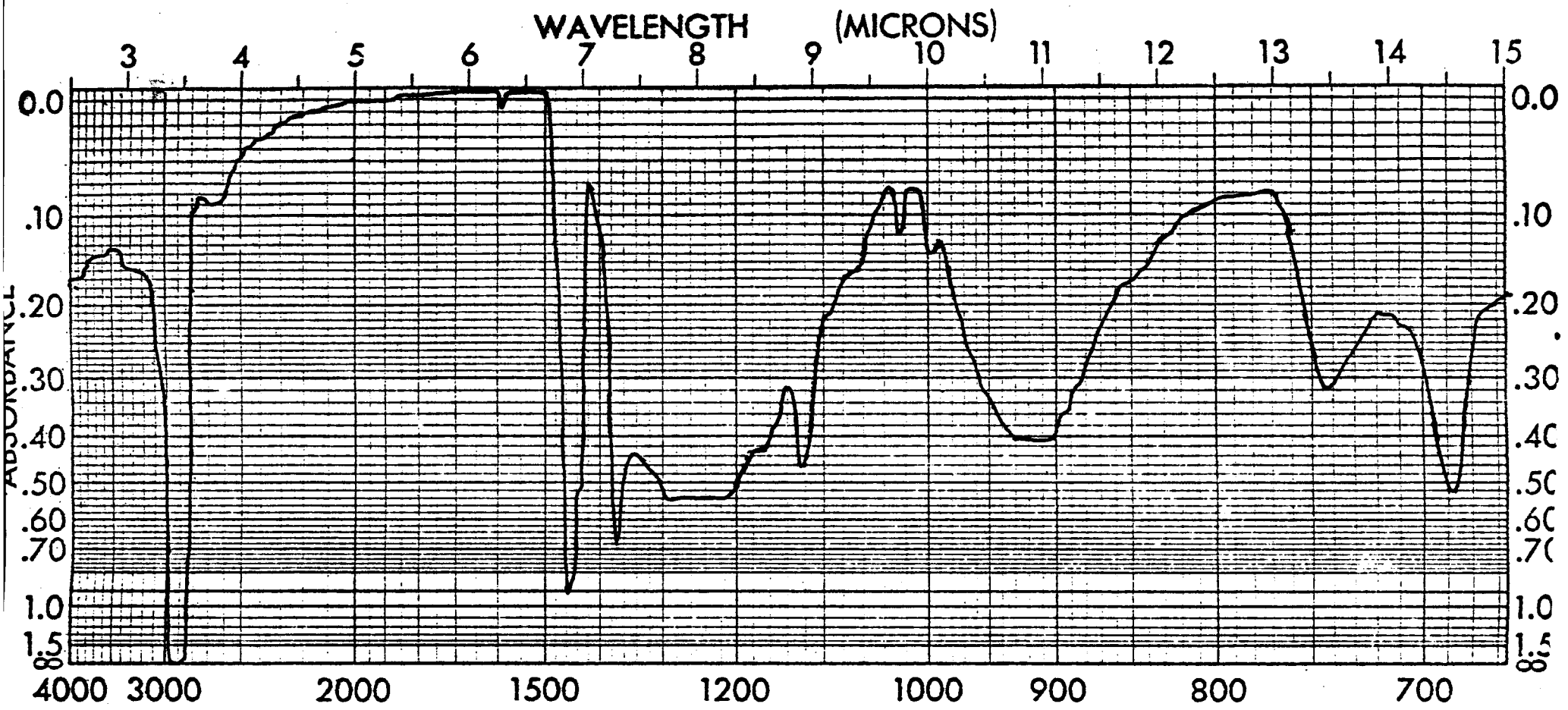


Figure 10

Infrared Spectrum of Product β-trans-[ØPN(NH_2)]$_4$ + $4CuSO_4.H_2O$ in Melt

AMERICAN INSTRUMENT CO., INC.
SILVER SPRING, MD.

CAT. NO. 4-4435
100 X 100 DIV.

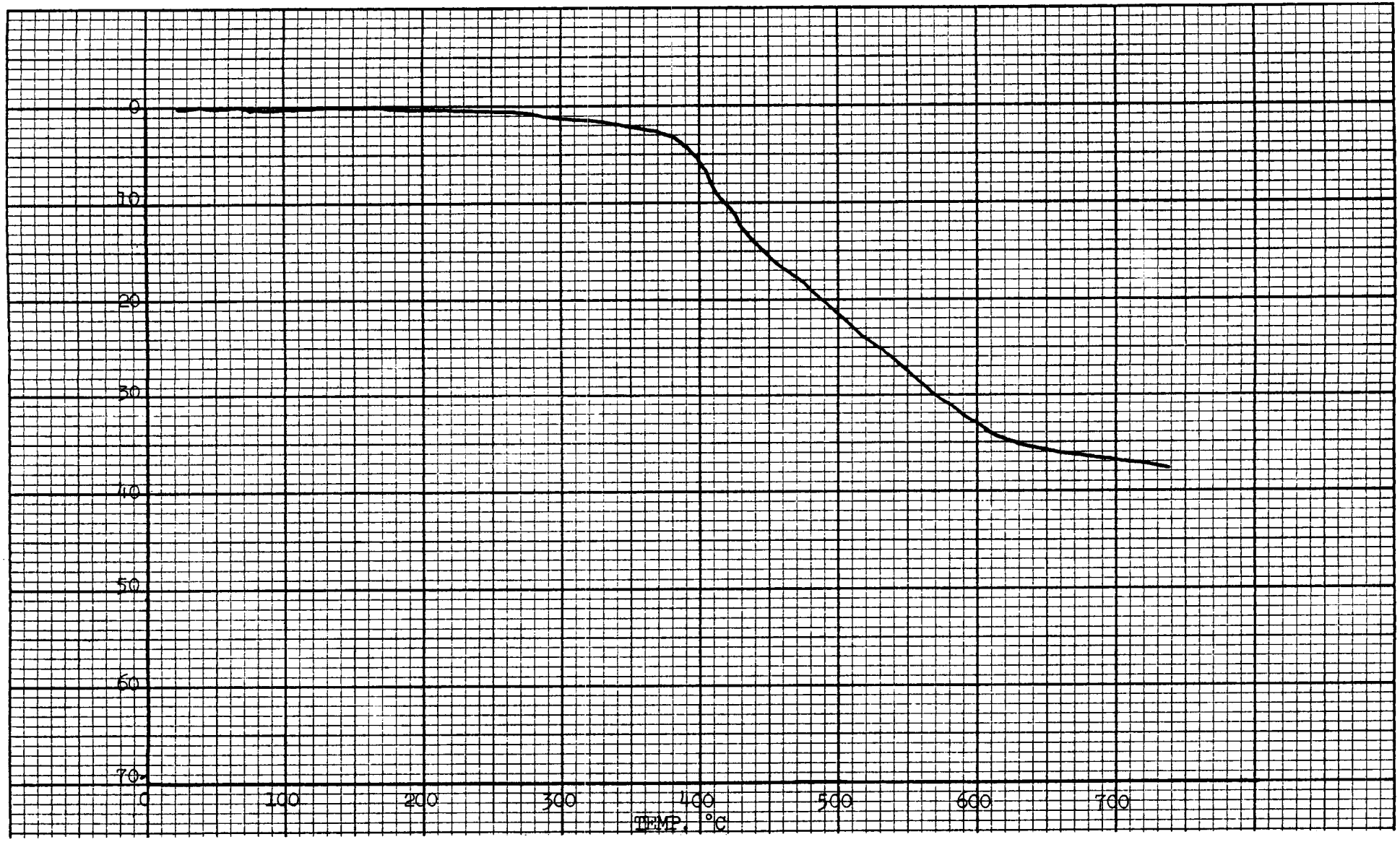


Figure 11

TGA of Polymer from β-trans-$[\emptyset PN(NH_2)]_4$ Heated 6°/Min in N_2 Stream

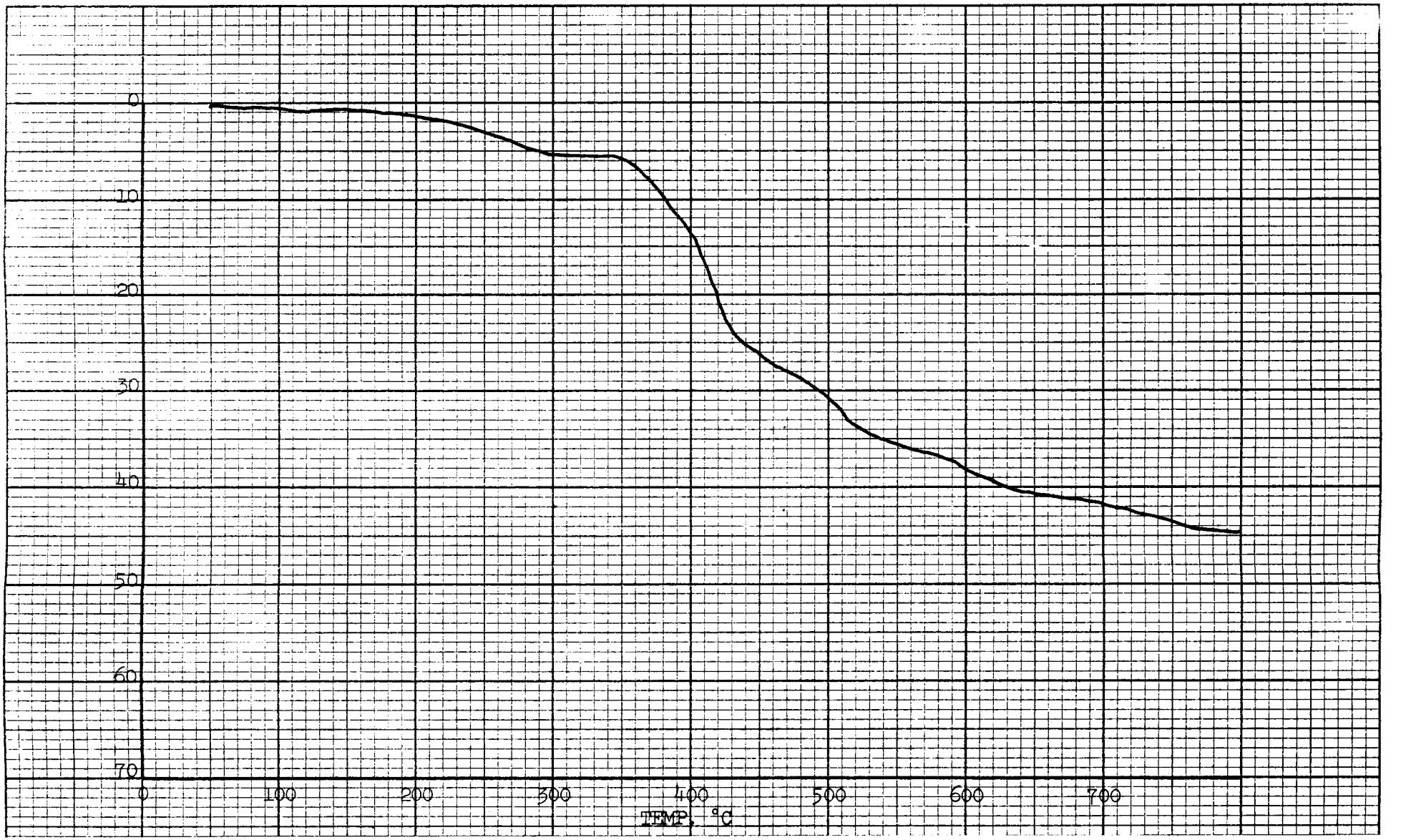


Figure 12

TGA of Complex $\left[[\emptyset PN(NH_2)]_4.(CuCl_2)\right]_n$ Heated 6°/Min in N_2 Stream

Figure 13

TGA of Complex $\left[[\phi PN(NH)_{.5}]_4 . CuCl_2\right]_n$
with Prior Deammoniation in Anisole Heated 6°/Min in N_2 Stream

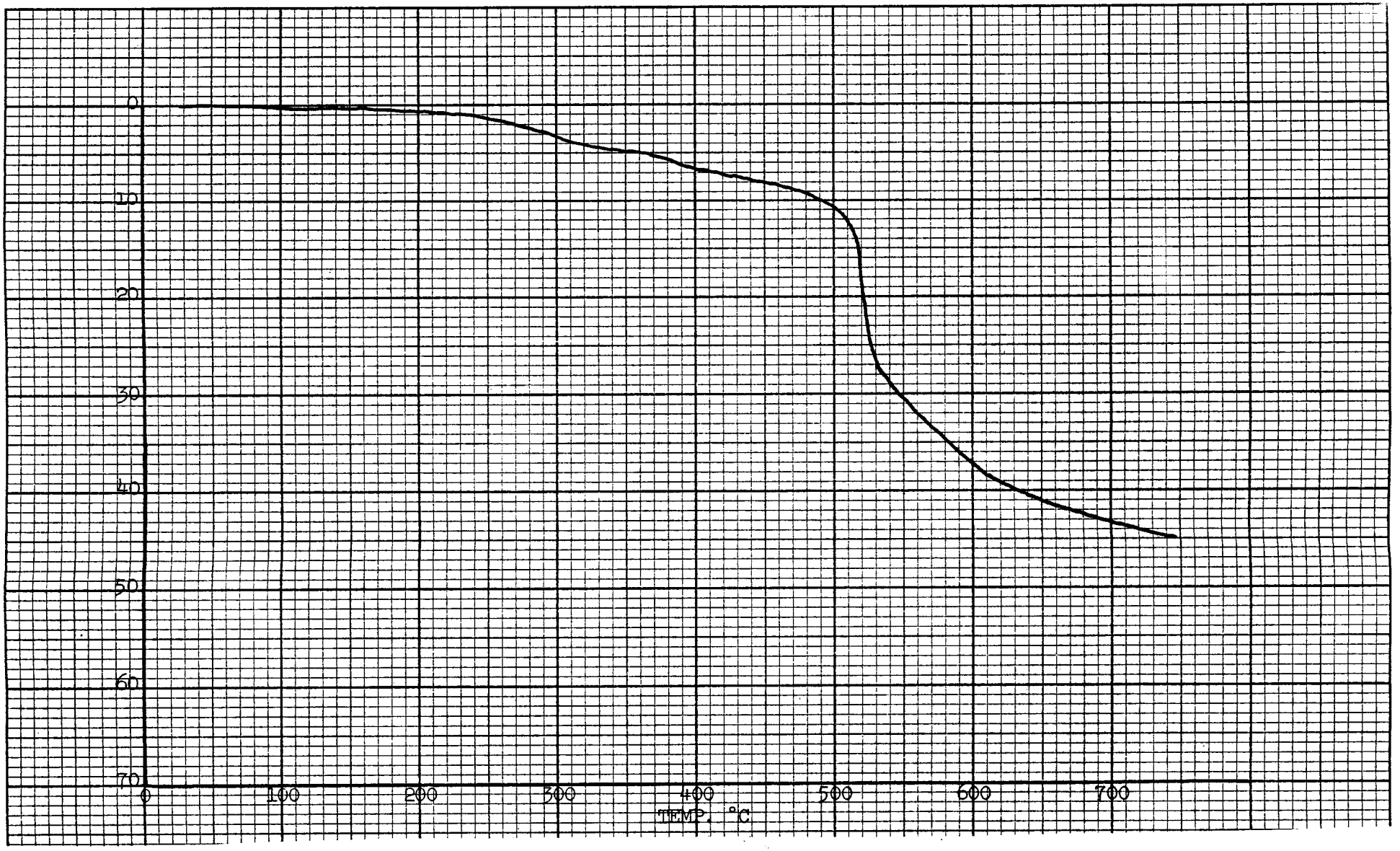


Figure 14

TGA of $\left[[\text{ØPN}(NH_2)]_4.CuSO_4.H_2O\right]_n$ Heated 6°/Min in N_2 Stream

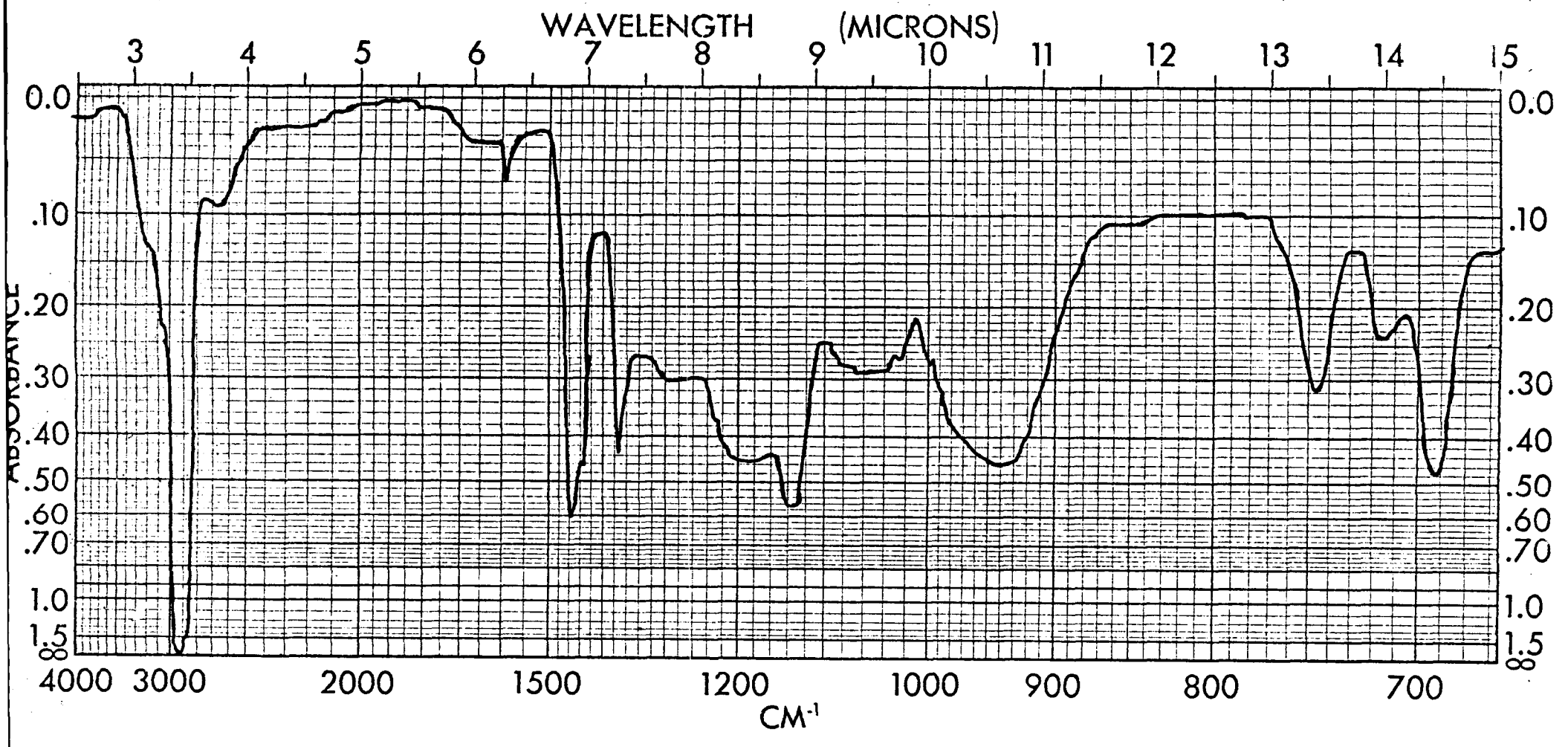


Figure 15

Infrared Spectrum of β-trans-$[\phi PN(NH_2)]_4.CuSO_4.H_2O$ After Deammoniation

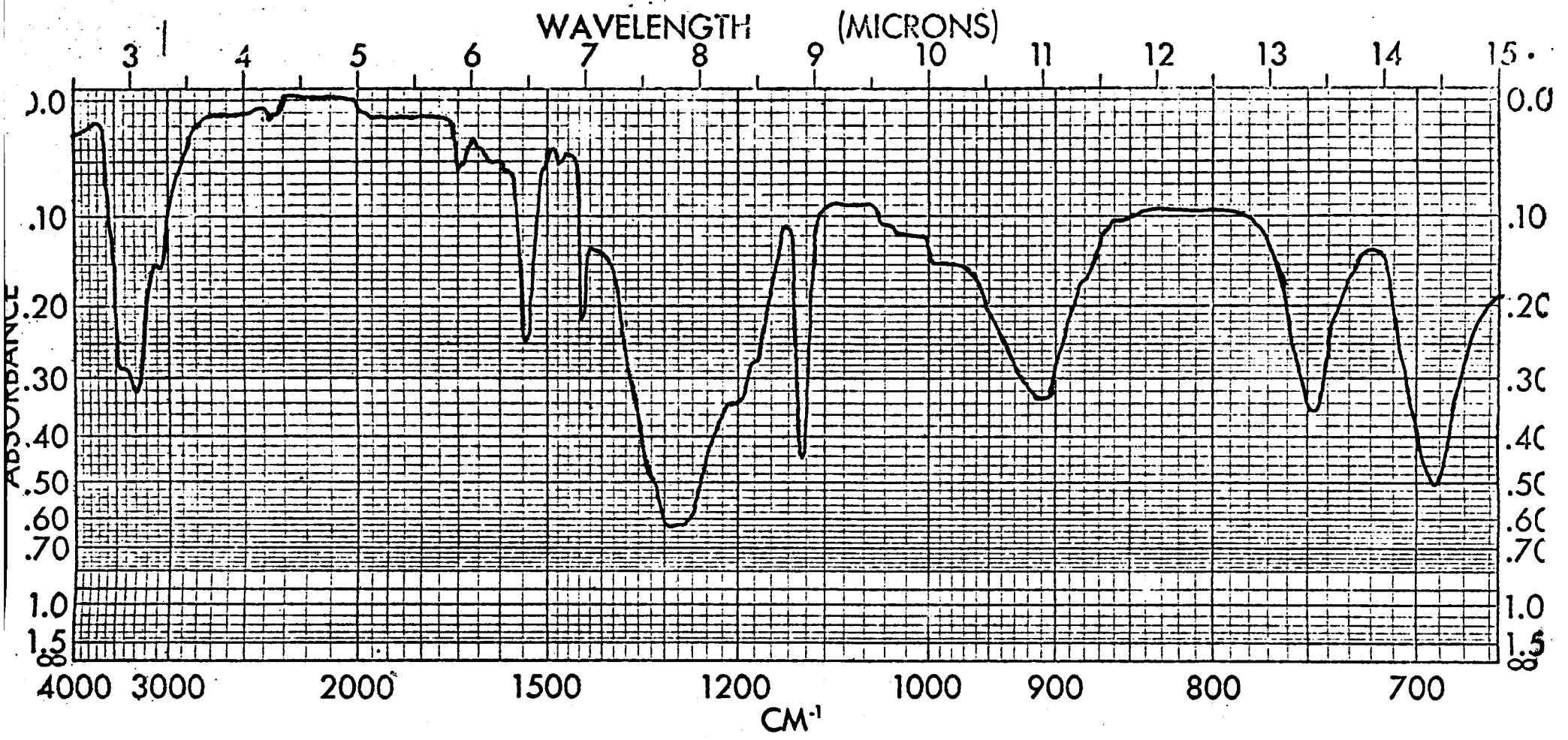


Figure 16

Infrared Spectrum of $[(\phi PNNH_2)_4.CoCl_2]_n$ Prepared in Acetonitrile

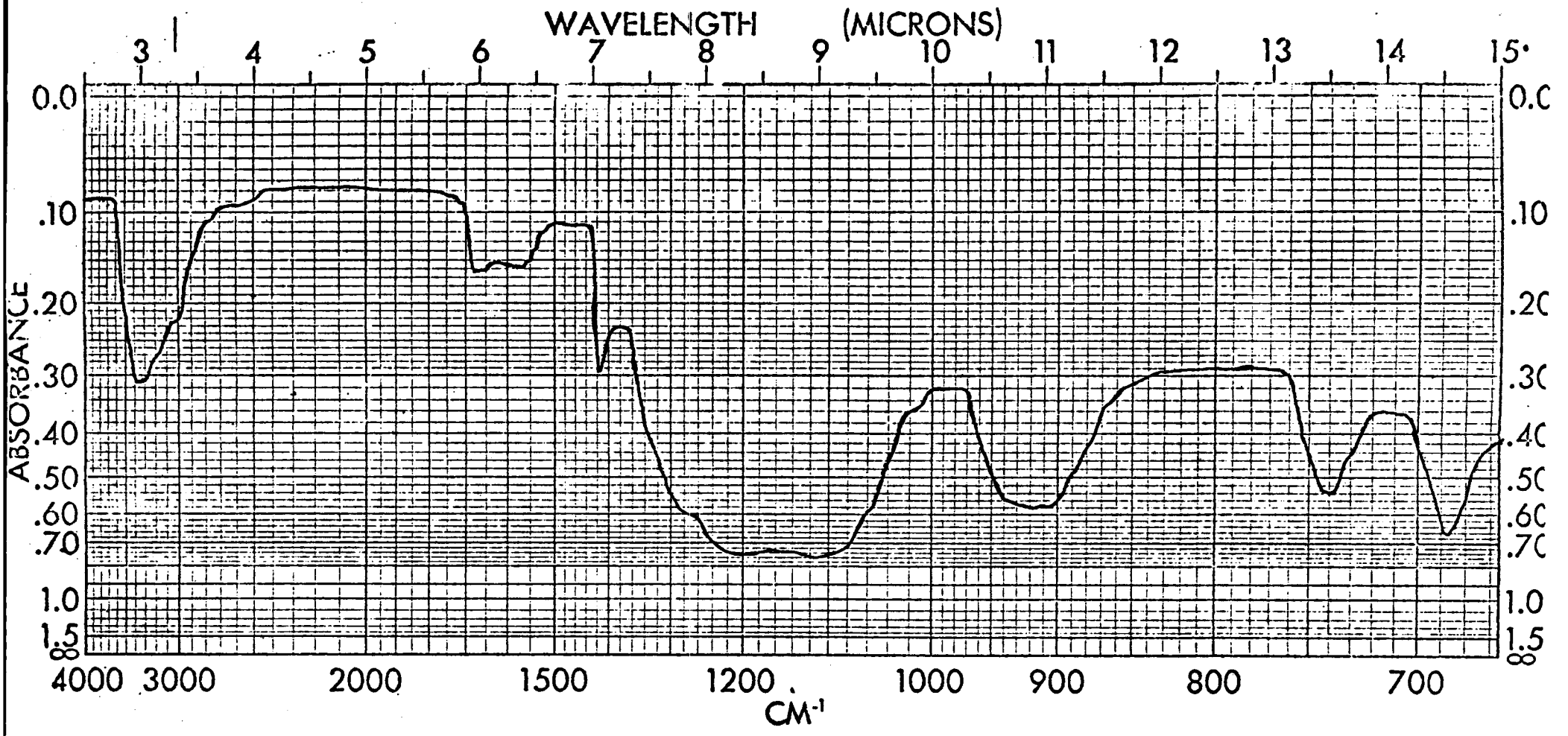


Figure 17

Infrared Spectrum of $[(\emptyset PNNH_2)_4.CoCl_2]_n$ Prepared in the Melt

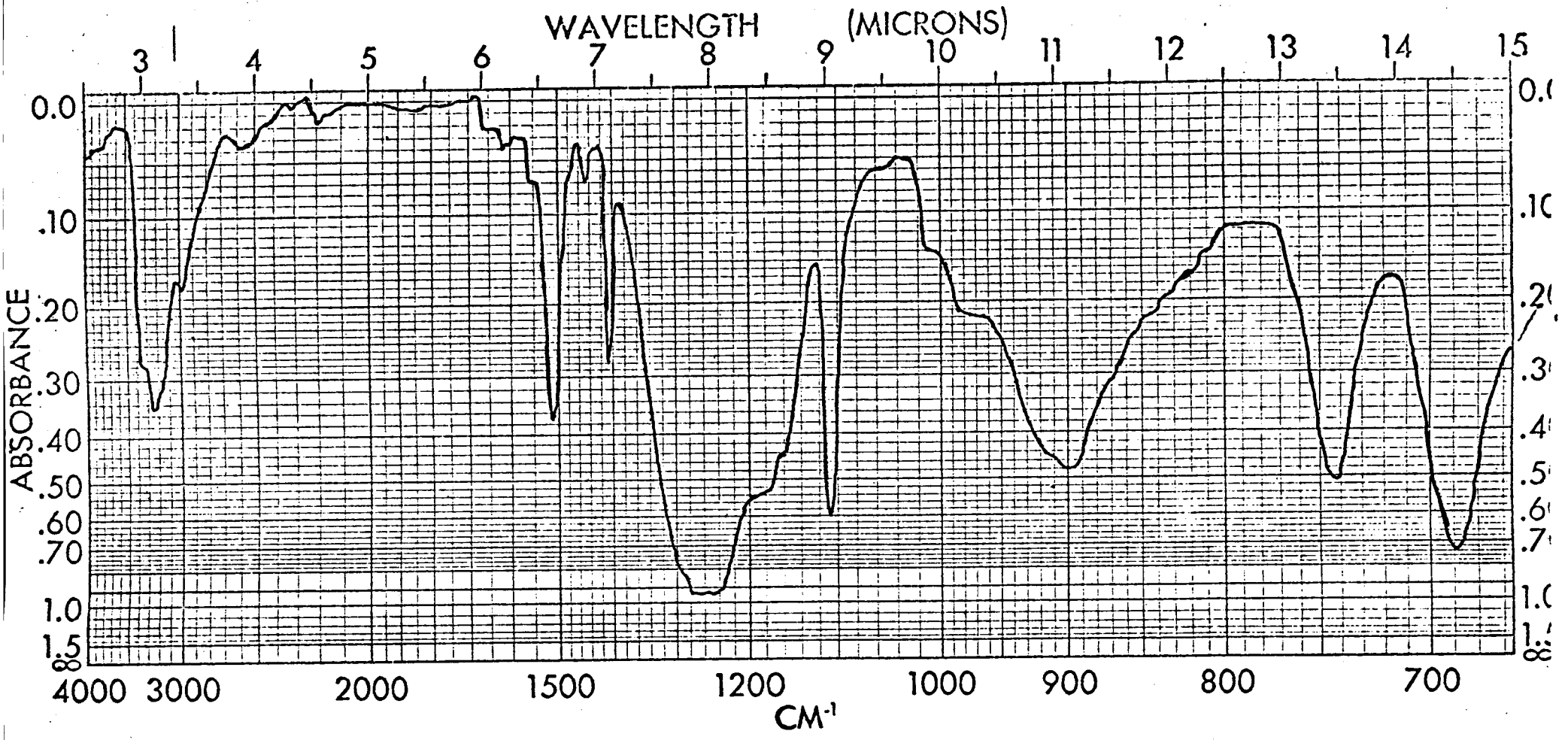


Figure 18

Infrared Spectrum of $[(\phi PNNH_2)_4.FeCl_2]_n$

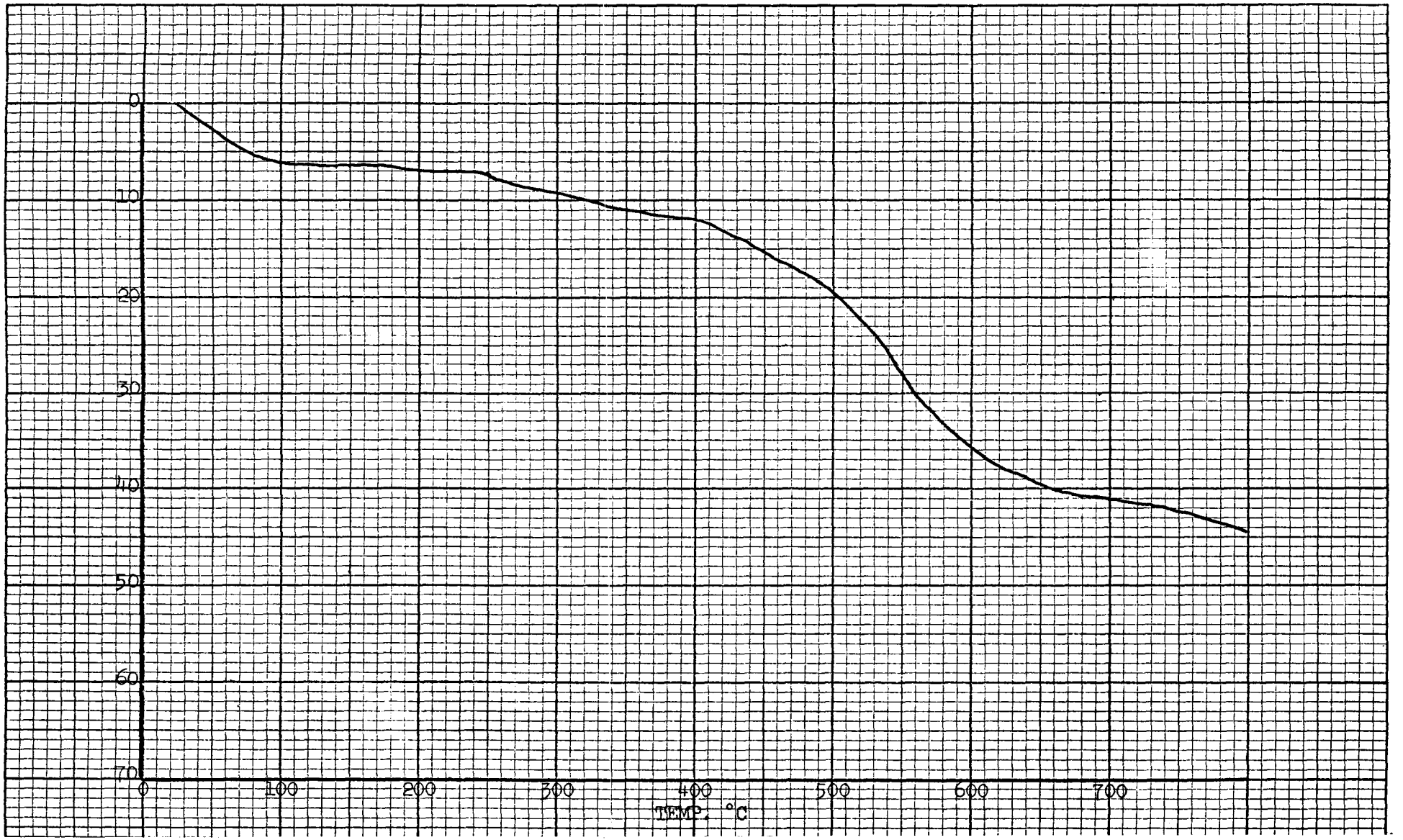


Figure 19

TGA of $\left[[\text{ØPN(NH)}_{.3}]_4\ (\text{CoCl}_2)_{.25}\right]_n$ Heated 6°/Min in N_2 Stream

REFERENCES

1. B. Grushkin, R. M. Murch, Second Annual Report, Contract No. NASw-924, SC No. 5743, Control No. 10-6098, Period of May 1965 to April 1966.

2. B. Grushkin, R. G. Rice, First Annual Report, Contract No. NASw-924, SC No. 5743, Control No. 10-2837, Period of April 1964 to May 1965.

3. Grundman and Raetz, Z. Naturforsch, 10b, 116 (1955).

4. Otto, Audrieth, J. Am. Chem. Soc., 80, 5894 (1958).

5. Tesi, Otto, Sherif and Audrieth, J. Am. Chem. Soc., 82, 528 (1960).

6. Sonntag, Chem. Reviews, 52, 237 (1953).

7. Shorts, Bilbo and Gentry, Inorg. Chem. 5, 2140 (1966).

DISTRIBUTION LIST - FINAL

Chief, Materials Research Branch (Code RRM)
National Aeronautics and Space Administration
Washington, D. C. 20546 (25 copies)

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812
Attn: R-P&VE-MNP (9 copies)

Director, Research SRT (Code RR)
National Aeronautics and Space Administration
Washington, D. C. 20546 (1 copy)

Dr. Bernard Achhammer
National Aeronautics and Space Administration
600 Independence Avenue, S.W.
Washington, D. C. 20546 (1 copy)

Mr. Elliott Bukzin, (Code 342A)
Navy Department, Bureau of Ships
Washington, D. C. (1 copy)

Mr. Sam A Marolo (MANC)
Research and Technology Division
Wright-Patterson AFB
Ohio 45433 (1 copy)

Dr. E. Kober
Associate Director of Research
Chemicals Division of Olin Research
Olin Matheson Chemical Company
New Haven, Connecticut 06701 (1 copy)

Dr. H. H. Sisler, Head
Department of Chemistry
University of Florida
Gainesville, Florida 32603 (1 copy)

Dr. George F. Pezdirtz
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23365 (1 copy)

Dr. John A. Parker
National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035 (1 copy)

Distribution List (Cont'd)

New Technology Representative (Code UT)
National Aeronautics and Space Administration
Washington, D. C. 20546 (1 copy)

Dr. Nathaniel S. Schneider
Materials Research Branch
U. S. Army Natick Laboratory
Natick, Massachusetts 01760 (1 copy)

Miss Dorothy Morris, Chief, Library
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135 (1 copy)

Covering Letter to:

Mr. Carl M. Grey
Contracting Officer
(Code BCB)
NASA Headquarters
Washington, D. C. 20546

DISTRIBUTION LIST - FINAL

Chief, Materials Research Branch (Code RRM)
National Aeronautics and Space Administration
Washington, D. C. 20546 (25 copies)

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812
Attn: R-P&VE-MNP (9 copies)

Director, Research SRT (Code RR)
National Aeronautics and Space Administration
Washington, D. C. 20546 (1 copy)

Dr. Bernard Achhammer
National Aeronautics and Space Administration
600 Independence Avenue, S.W.
Washington, D. C. 20546 (1 copy)

Mr. Elliott Bukzin, (Code 342A)
Navy Department, Bureau of Ships
Washington, D. C. (1 copy)

Mr. Sam A Marolo (MANC)
Research and Technology Division
Wright-Patterson AFB
Ohio 45433 (1 copy)

Dr. E. Kober
Associate Director of Research
Chemicals Division of Olin Research
Olin Matheson Chemical Company
New Haven, Connecticut 06701 (1 copy)

Dr. H. H. Sisler, Head
Department of Chemistry
University of Florida
Gainesville, Florida 32603 (1 copy)

Dr. George F. Pezdirtz
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23365 (1 copy)

Dr. John A. Parker
National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035 (1 copy)

Distribution List (Cont'd)

New Technology Representative (Code UT)
National Aeronautics and Space Administration
Washington, D. C. 20546 (1 copy)

Dr. Nathaniel S. Schneider
Materials Research Branch
U. S. Army Natick Laboratory
Natick, Massachusetts 01760 (1 copy)

Miss Dorothy Morris, Chief, Library
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135 (1 copy)

Covering Letter to:

Mr. Carl M. Grey
Contracting Officer
(Code BCB)
NASA Headquarters
Washington, D. C. 20546